REPORTS

OF THE

PROGRESS OF APPLIED

CHEMISTRY

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PREFACE.

THE various sections of these Reports now cover the whole range of subjects dealt with in the Society's Journal. Reports on Explosives and on Analysis appear for the first time, the former dealing with the literature of the period from the beginning of the war to the end of 1919 so far as it is available.

The Reports on Ceramics, Building Materials, and Fermentation for 1918, held over from Volume III, are also included, together with the Reports on these subjects for 1919.
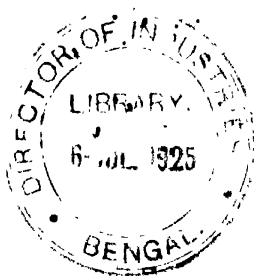
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REPORTS

OF THE

PROGRESS OF APPLIED CHEMISTRY.

PLANT AND MACHINERY.

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THE conclusion of the armistice on November 11, 1918, re-acted power-fully on the manufacture of plant and machinery for chemical industries. The large Government plants erected during the war for the manufacture of acids, low and high explosives, poison gases, and other military necessities of a chemical nature were shut down a few weeks after the cessation of hostilities, and their large stocks of acids and other materials were placed on the general market, as also were huge quantities of plant, such as engines, dynamos, alternators, pumps, retorts, stills, filters, condensers, sulphonators, nitrators, etc. In like manner many private firms who provided explosives and other chemicals for the Ministry of Munitions, and who in most cases produced the nitric and sulphuric acids necessary for the manufacture, had to stop making materials for war, either shutting down acid plants entirely or curtailing their activities to an extreme degree.

The result of this was a long period of stagnation. Nitric acid was required principally only for nitrobenzene and nitrotoluene, dinitro-benzene and dinitrotoluene There was comparatively little acid to be treated for denitration and concentration, and manufacturers had on their hands a very large surplus of plant of all kinds for these opera-tions. No wonder that makers of chemical plant have complained throughout the year of the tremendous slump in trade.

Other industries, not purely chemical, have also been seriously affected. For example, coke-oven works and gas works which, in almost every case, during the war were obliged to take measures to extract benzene and toluene from coal gas in order to supply the primary materials for the manufacture of picric acid and trinitrotoluene

and which also in many cases undertook to make and supply pure, strong
ammonia liquor for the production of ammonium nitrate, had to choose
whether they stopped these processes, or continued to make ordinary
benzol for motor spirit and dye-making works, and ammonia for pur-
poses other than explosives. As a matter of fact nearly all the coke-
oven works continue recovering benzol as before the war, and several
large gas works have decided to keep on their new plants. It is probable
there are very few plants continuing to make strong, pure ammonia
liquor, however. In not a few instances second-hand gas washers and
other appliances have changed hands during the year.

Taking the situation as a whole, it can be said that surplus of plant
and all kinds of spares has been so great that comparatively few orders
for new plant were placed until the year was well advanced, and then
unfortunately the moulders' strike, starting as it did in September last,
absolutely stopped the manufacture of castings of every sort, thus
further jeopardising progress. At the time of writing, this strike is not
yet settled, and it is difficult to see how many chemical manufacturers
could have carried on as well as they have done, had it not been for the
slackness in trade and the large accumulations in plant and machinery
throughout the country. Manufacturers of acid-resisting metals,
silica-ware, chemical pottery, and brick linings, who responded so well
to the heavy calls made on their resources during the war, have been
hard hit. These manufacturers can in some cases revert to peaceful
pursuits. The Thermal Syndicate are, for example, turning their
wares into laboratory apparatus, electric insulators, furnaces, lamp
globes and shades and such like, whilst some pottery makers who
turned out quite good chemical earthenware have reverted to the
manufacture of articles for common use, such as jam pots, etc.

The large and costly Government plants erected for the manufacture
of oleum have been at a standstill and no one seems to know what is to
become of them. Unfortunately they were designed for the catalytic
oxidation of the sulphur dioxide obtained by the burning of arsenic-
free sulphur, and their conversion into pyrites-burning plants would
certainly not be attended with anything like the success they enjoyed
while burning sulphur. However, it seems a pity to see them lying
idle when the sulphuric acid supply of the country is beginning to show
signs of failing to suffice for all needs.

Again, it is almost to be regretted, from a purely chemical point of
view, that circumstances arose which prevented the continuation of
the important work started in this country on the fixation of nitrogen
and the oxidation of ammonia on a large scale to nitric acid. A dozen
or so small plants were put into operation in the North of England by a
Yorkshire firm during the past eighteen months for the oxidation of
ammonia to nitric acid in the manufacture of chamber sulphuric acid,
this system having been recommended by the Ministry of Munitions as

a substitute for the ordinary method of distilling nitric acid from nitrate
of soda, in order to conserve the supplies of the latter. These plants
have worked well, it is stated, but whether they will continue to be in
demand or not will no doubt depend on the respective market prices
of ammonia, sodium nitrate, and sulphuric acid. To describe the plant
briefly. The air and ammonia mixture, containing about 10% of the
latter, both gases being metered by rotary meters, is conveyed through
cast iron pipes. It is usual to filter the air by drawing it through a
steel box containing wood wool. The mixture then passes through
platinum gauze. This gauze consists, in the case of small units, dealing
with the equivalent of $1\frac{1}{2}$ cwt. of sodium nitrate per day, of one rectangu-
lar piece, 18 in. by $6\frac{1}{2}$ in., folded into four so that its dimensions are
$4\frac{1}{2}$ in. by $6\frac{1}{2}$ in. It is made of wire 0·0025 0·003 in. diameter, and there
are 80-100 meshes to the linear inch. The gauze is tied across its
surface by two or three strands of the wire, and is placed between two
washers of asbestos board, or better, nickel-chrome sheet, which fit the
small converter chamber. To start working, the gauze is first heated
by a plumber's blow-pipe; afterwards the reaction keeps it at a cherry
red. The rotary meter for the air should have a capacity of at least
2000 cubic feet per hour. The mixture of gases is pushed through by
means of a low-pressure fan blower capable of working against about
8 inches water pressure. The small converter chamber was at first
made of aluminium or enamelled iron, but cast iron has been found to
answer better. After the converter comes a small cooling system,
consisting of four horizontal lengths of 2-in. silica pipe and an earthen-
ware drip pot. The apparatus is very simple. The chief trouble is
the usual one with catalysts—they do not last for ever.

Another factor which must have had a strong influence on the trend
of opinion regarding the real utility of new appliances, patented or not,
designed for labour saving, is the steady rise in wages that has been
taking place during the last three or four years, a rise which even yet
does not appear to have reached finality. Factory owners are obliged
seriously to think of the cost of handling materials of all kinds. Labour-
saving devices which were formerly ruled out of court, on account of
heavy initial expenditure as well as high repairs and maintenance
costs, have now been reconsidered. Unfortunately, the prices of iron
and steel, crude and finished, have also gone up to astonishingly high
figures, while the cost of spare parts and mechanics' wages have kept
pace with them. On the whole, however, there is, and will be, a
greater tendency in chemical factories than formerly to displace ordinary
labour by machinery, and, further, a greater amount of study will be
given to the design and guarantees of any new apparatus put in. The
present prices of industrial coal—about three times what they were
before the war—are also compelling chemical manufacturers to join
heartily in the general crusade against waste of fuel. Apparently as a

result of these influences, large water-tube boiler installations of the best kind are being introduced in some big works, with all the accessories mechanical stokers, economisers, superheaters, feedwater heaters, circulators that make for fuel economy. There is no doubt that water-tube boilers gain a few points in thermal efficiency over the ordinary Lancashire type if the water is at all suitable or can be made suitable by softening plant, though most engineers prefer the latter for ease of running and maintenance. In so e large installations known to the writer, pneumatic (vacuum) handling of the clinker and ash is resorted to in order to save labour, and, while the coal supplied remains in its present very "dirty" condition, containing as it does a large proportion of bats and dross, such a scheme will no doubt be very profitable. The large clinker is broken up on grids and is carried away with the ashes through iron pipes, by suction produced by an exhauster of the Roots type, to a common overhead storage bunker whence delivery is made by gravity into railway wagons. There is heavy erosion of the pipes at bends or corners, and there it is necessary to increase the thickness of metal and preferably to use the harder manganese steel. Capital charges, power, and maintenance total up to a high figure 2s: 6d. per ton of ash or more unless the plant is a very large one, or the coal is very high in ash.

In the production of electricity on a large scale, say 1000 kilowatts and over, steam turbines find most favour in modern works, and on a chemical works where there is a demand for low-pressure process steam the turbine is so designed as to work condensing or non-condensing automatically, and to part, on the low-pressure side, with a portion or all of its steam at any desired pressure (20 40 lb. is usual) suitable for long-distance transmission. In this way, the turbine acts as a governor or steam-reducing valve, and the low-pressure steam sent to do process work usually retains about 95% of its value as a heating agent. When the steam is supplied to the turbine superheated, as it ought to be, the low-pressure steam will leave the turbine with sufficient superheat to carry it long distances at least a quarter of a mile—without any loss in condensation, provided first-class insulation of the steam piping is provided. When there is a large demand for low-pressure steam, such as, for example, in the case of the manufacture of Mond gas with ammonia recovery where the steam entering the producers need have a pressure of only a pound or two per square inch, it is by far the most economical plan to utilise steam engines instead of electric motors to provide mechanical energy, and to work them non-condensing, sending the exhaust steam to do the process work where it is the latent heat which mainly counts. In this way the steam consumption for a given horse-power is reduced to about one-fifth or one-sixth of what it would be were condensing engines used and high-pressure steam supplied to the process. One thing that is sometimes overlooked is the necessity

ot providing large enough mains and services to carry the low-pressure steam. If this point is not attended to the process may suffer in the rate of heating. The above principle of aiming at using steam for a double purpose is a strong argument in favour of the water-tube boiler, which will work safely at 250–300 lb. pressure as against 150–170 lb. for the Lancashire.

The opening of the world-renowned German chemical factories, situated on or near the Rhine, to the inspection of the Allies under the terms of the armistice gives us a welcome insight into the progress made in chemical plant and machinery by our late enemies, not only during the years of war, but also during many years that led up to the outbreak of war. The written and verbal reports that have come from chemical and engineering experts who visited the German chemical works in the Rhine valley, when summed up, lead to several important conclusions. The plant and machinery and general equipment of these great factories are much more immense in extent, and more complete in every detail, than they were before the war. In making the large additions to plant' for the purpose, in the first place, of providing munitions of war, there was always in evidence the strong ulterior motive of placing the German chemical industries in a position of so greatly enhanced superiority as to make them practically invincible in the coming competition for the world's trade in chemicals of all kinds, unless steps should be taken by the Allies to build up and foster on a proper scale their chemical undertakings, especially those connected with fine chemicals, dyestuffs, and general organic products It is not so much that the German apparatus and machinery are superior to ours, for it is generally agreed that we have not lagged very far behind in this respect Nor have we much to learn from the Germans in the methods of handling materials on a large scale, in steam and electricity generation, or gas manufacture, or in the transport or transmission of steam, electricity, water, gas, or acids. It is rather that German chemists during all these years of experience and monopoly in the manufacture of numerous chemical products have been evolving the types of plants most suitable for their respective purposes, and now have at their command working, or ready to work on short notice, all the large-scale apparatus they require for the production of enormous quantities of guaranteed pure and standardised chemicals, which will satisfy every reasonable requirement. whereas countries like our own have still to plough the lonely furrow of investigation and research, as well as design, and erect plants sufficiently large to give us anything like a chance of competing in the fine chemical trade.

In other words, we have our fair share of engineers, and engineering knowledge and experience, but we are woefully lacking in well-trained chemists, chemical research and chemical engineering experience of the best kind. There are those who maintain that the chemist had in the o"

past too much voice in the design of chemical plant in Germany, and
that this accounted for a certain lack of progress in plant design that
might otherwise have been anticipated. "They point to the more recent
installations as evidence of a freer hand for the mechanical and con-
structional engineer. It can be said without fear of contradiction that
the German chemical industries retain their high reputation for the
quality and finish of their plant and machinery, and for the careful
attention paid to their maintenance, and to every detail of process
working. While our engineering firms have succeeded fairly well with
castings for retorts, stills, etc., and can cope with steel work of all kinds,
they are still a long way behind Germany in the satisfactory enamelling
of apparatus to resist acids and in the casting of large vessels of
silicon-iron. In some of the German works there are in use vessels of
silicon-iron 7 feet in diameter and 2 inches thick. Large pots of special
stoneware are in common use for the transport of acids, and enamelled
drums are employed largely for carrying oleum, and thus a purer pro-
duct can be delivered than is possible when ordinary steel tank wagons
are employed. Furnaces on the German works, as far as we can learn,
are of quite a simple design, producer gas, generally made without
ammonia recovery, or water gas being employed as heating agent.
The gas producers have, for the most part, mechanical rotary hearths
and work with brown coal. Steam plant is of quite ordinary type,
Lancashire boilers working at 100 lb. pressure without superheaters
being the general rule. Electricity is mostly generated by steam
turbine and is usually three-phase. The electric motors are also three-
phase as a rule, rotary converters being installed only when direct
current is required for electrolytic processes, such as chlorine manu-
facture. In filtering operations very large filter-presses of the well-
known Dehne type are still in common use. The plates are sometimes
as large as 5 feet square, and hydraulic pressure is used in closing the
presses. It is also a common practice after filter-pressing to drop the
cakes into a tank, mix into a slurry again, and re-filter, this being done
to effect better washing of the cake. Owing to the dearth of suitable
filter cloth during the war, vacuum filters have had to be largely resorted
to, the filtering medium being porous clay tiles. As drying apparatus,
the Passburg vacuum dryer is still in favour. Hot water under pressure
is sometimes used as the medium of heating for the sake of better con-
trol. The novel Huillard apparatus is sometimes applied to pasty
masses. This consists of a long belt conveyor made of wire woven like
a wire mattress. The paste is forced into the interstices and carried up
a shaft through which hot air is passed ; on its return journey the dried
solid is knocked out by tapping. Evaporators appear to be mostly of
the vertical long-tube type worked in double or quadruple effect.
Grinders are of many different patterns to suit conditions. It is note-
worthy that Krupp & Co. obtained special steel for making the ball

mills, which they turned out in large numbers before the war, from Hadfield's of Sheffield.

In the complete removal of dust from gases, the modern German works have paid special attention to electrostatic deposition. Thus, the latest oleum plants combine the advantages of Cottrell electrostatic precipitators with simplification of the filtering apparatus, the cumbersome coke or quartz filters usually found on oleum plants being almost entirely dispensed with Some of these plants are of American design and must have been erected not long before the war started. The efficiency of removal of dust carried by the gases leaving the pyrites burners requires to be very complete (99·99% is not good enough) if the platinum contact masses are to retain their activity for years. The precipitators are therefore of ample size and so arranged as to stop the pyrites burner if the high tension electrical supply should fail.

Turning now to the inventions of chemical plant and machinery of the past year, as recorded in the literature, it may be said that if there has been a want of progress in the construction of new plant there has been no lack of ideas for improvements. There are over 550 patents dealt with in the Journal under Section 1 (Plant and Machinery) for 1919, being about 25% more than the previous year. Were it not for unavoidable delay in publishing patents one would expect to find a diminution in the number instead of an increase, owing to the well-known fact that during the war many teachers of chemistry and other chemistry students took up duties as works' chemists, and many of these returned to their former duties when the Government and other plants providing explosives, etc., were shut down.

The subject of furnaces claims the largest number of patents, and will no doubt continue to do so having regard to the importance of coal conservation. It is a very difficult matter to adjudicate on the merits of the various proposals, an actual working trial being in most cases the only test. There are several designs of regenerative furnaces but nothing calling for special note. A regenerative muffle furnace, patented by T. W. S. Hutchins,[1] is arranged in a remarkable way, six muffles being fixed in a circle round a gas producer. Valves are provided so that each muffle chamber may be connected with the adjacent chamber or with a passage leading from the producer. Valves are also provided controlling air inlets to the muffle chambers and outlets to the flue. The furnace is to be worked so that one muffle at a time is opened for discharging and recharging, and the air supply for the working muffles is heated by passing through two chambers. A furnace for the use of liquid fuel has been patented by D. Wright,[2] and one by A. E. Windle,[3] and there are others for the use of powdered

[1] Eng. Pat. 120633; J., 1919, 1A.
[2] Eng. Pat. 125629; J., 1919, 397A.
[3] Eng. Pat. 13_25i; J., 1919, 89IA.

fuel.[4] E. Podszus [5] describes what would appear to be a useful small-scale furnace for temperatures ranging up to nearly 2500° C. ; this is made of blocks of fused zirconia freed from iron. about 1% of boric acid being added to facilitate the binding of the blocks when heated. Gas burners are used, the orifices being made of well-burnt zirconium oxide. The burners are supplied with air or oxygen under pressure, heat recuperation being obtained by coiling the supply pipes in the space surrounding the furnace.

A furnace has been patented by N. Testrup [6] which consists of a flat, horizontal chamber provided with a conveyor for carrying material, such as coal, through the furnace.

Suggested improvements in drying apparatus form the subject of some seventy patents, notices of which appear in the Journal. A simple method of treating sludges is patented by A. P. Laurie.[7] The slurry is frozen, and then thawed, and the liquid allowed to drain away. Precipitated pigments treated in this way dry to a powder and not in cakes or lumps.

An interesting drying apparatus is that patented by M. F. Loewenstein.[8] It consists of a number of conveyors arranged one above the other in a casing. Between the carrying and idle halves of each conveyor are placed horizontal pipes conveying hot waste gases ; these pipes are enclosed by plates forming chambers through which air can be blown, the air leaving through perforations in the upper plates immediately under the material to be dried. A somewhat obvious method of drying is that proposed by L. R. Christie,[9] who passes hot gases first along the outside of a double-walled rotary drum and then through the inner shell, the material to be dried passing through the annular space. What looks like a useful apparatus has been patented by C. H. Meister.[10] This is said to be suitable for liquid, semi-solid, or solid material. The reader must be referred to the full description.

Several papers on filtration have been read during the past year. That of L. Fabre [11] gives a very useful account of the modern methods. In France continuous rotary drum filters are in common use for ordinary sludges, rotary drums with drying sieves for crystals, or rotary clarifiers. In this country we adhere to the old-fashioned filter-press, while in America open tank filters are in greatest favour. The ordinary rotary filter is rotated, half submerged, in the tank containing the mud to be

[1] Eng. Pat. 120212 ; J., 1919, 449A.
[5] Z. angew. Chem., 1919, 32, 146 ; J., 1919, 449A.
[6] Eng. Pat. 129758 ; J., 1919, 670A.
[7] Eng. Pat. 121372 ; J., 1919, 61A.
[8] Eng. Pat. 126748 ; J., 1919, 450A.
[9] U.S. Pat. 1318133 ; J., 1919, 885A.
[10] Ger. Pat. 312424 ; J., 1919, 854A.
[11] Chim. et Ind., 1919, 2, 759 ; J., 1919, 703A.

filtered, which is constantly agitated. The application of a vacuum causes a cake to form on the surface immersed, the liquor passing through the cloth to the central valve. The surface of each section can be sprayed with washing liquid as it rises, and the cake can be removed by compressed air or scraped off as it descends on the other side. A rotary filter, 6 feet in diameter and 3 feet wide, is capable of dealing with 30 tons of dry calcium carbonate from a caustic soda plant per day of ·24 hours.

Open tank filtration has already been briefly referred to. The filtering apparatus used consists of a number of filter leaves (tubular frames covered with filter cloth) suspended from an overhead travelling crane. The interior of each leaf can be put into communication with either a vacuum pump or a supply of compressed air. The leaves are first dipped into the tank containing the mud to be filtered and a vacuum is applied. When the cake is sufficiently thick, the leaves are lifted out and dipped into a tank containing the washing liquid which is drawn through. The leaves are again lifted out and suspended over the sludge tank, and the cakes are removed by compressed air blown through the interior of the leaves. It is usual to employ canvas cloths for neutral and alkaline liquids, Monel metal gauze for very caustic liquids, and woollen felt for acids. The filter leaf type is specially suitable for metallurgical operations, and in the latest designs can be used to filter under pressure, as well as vacuum, by enclosing the tank. Attention may be drawn to the compressible frames patented by J. Turner and R. G. Parker,[12] which are designed to permit the squeezing out of water from the filter cake by hydraulic pressure The mechanical difficulties in this case seem rather great.

Finally, the new filter plate designed by W. Furness [13] is worthy of note as we believe this is finding considerable scope. In this design filter panels of earthenware, or other acid-resisting material, are enclosed by the frame. The panels have vertically grooved surfaces, the lower ends of the grooves communicating with the discharge channels. Parts of the frame exposed to the action of acid are protected by lead or other suitable covering.

Wooden filter presses can be used with sulphuric acid liquors up to an acidity of about 30%, but maintenance is heavy.

Amongst patented novelties in crushing and grinding only two or three designs appear to merit attention. A grinding machine brought out by F. W. Lyon and A. Ross [14] consists of a cylinder, having a rotating cage, provided with radial slots. Grinding rollers are carried by links the ends of which can be pivoted at any point in the slots. The ground material is discharged through a grid occupying about 30%

[12] Eng. Pat. 123589; J., 1919, 41A.
[13] Eng. Pat. 124974; J., 1919, 315A.
[14] Eng. Pat. 121206; J., 1919, 35A

of the circumference of the cylinder, and a slight vacuum is maintained in the discharge conduit. Air is admitted into the cylinder and passes through to the outlet periodically, so that heavier material may fall back from the discharge conduit into the grinding cylinder. The shaft is mounted so as to allow of vertical movement when material accumulates in the bottom of the cylinder.

The ball mill of C. Candlot [15] is divided into two compartments, separated by a sifting device. The preliminary grinding is done in the first compartment ; the material then passes to the sifting device, which consists of superposed screens arranged in the form of a cone and shielded from the action of the balls. The fines pass through to the finishing compartment and the coarse portions are returned to the first.

A rotary pulveriser, patented by A. E. Davis,[16] is provided at one or both ends with a chamber divided into two compartments by a screen. A current of air is used to carry the finer particles through the screen, blockage of which by the coarser particles is prevented by a projecting disc, carrying vanes, which is rotated close to the screen.

There are comparatively few new patented ideas on the subject of cooling and condensing, and there is nothing which we think calls for special remark.

In general washing apparatus, C. H. Borrmann [17] gives an account of the remarkable success attending the use of Kubierschky's system of spraying columns for washing gases with liquids, or one liquid with another (immiscible), and in distilling, tar separation, cooling, etc. Chemical manufacturers might well adopt a more progressive attitude in gas washing. Sometimes, half a dozen cumbersome towers, filled with coke or other packing, are erected for the extraction of ammonia or benzol, or other vapours, giving poor results and setting up heavy back pressure, when a single modern spray washer would do the work more efficiently and with practically no back pressure.

For the fractional distillation of mixtures of liquids which are miscible with water, for example, light tar oils, A. Goyvaerts, P. Becquevort, and H. E. Bossut [18] have patented a continuous method. The mixture of liquids is fed into the first of a series of stills to which open steam is supplied. Steam and oil vapours pass on and are fractionally condensed in the next still, and so on ; the vapours from the last still pass through a condenser. It is claimed to obtain by one distillation of crude benzol, commercial benzol from the condenser, commercial toluol from No. 3 still, naphtha from No. 2 still, and creosote from still No. 1

Eng. Pat. 115624 ; J., 1919, 661A.
Eng. Pat. 128071 ; J., 1919, 561A.
Z. angew. Chem., 1919, 32, 149 ; J., 1919, 521A.
Eng. Pat. 120940 ; J., 1919, 62A.

There are over a dozen patents of improvements in refrigerating apparatus and a similar number relating to centrifugal machines.

Electrostatic deposition of dust from gases has been receiving serious consideration during the past year or two, and has already been applied in a few instances to the separation of solid matter from blast furnace gases. A large new installation, designed by the Lodge Fume Deposit Co., is about to be started by the Skinningrove Iron Co. E. E. Thum [19] recommends that in large plants the precipitators should be divided into independent sections, each fully equipped with transformers, rectifiers, etc. He suggests the necessity of ensuring that the precipitated material should be rendered conducting by adding a dust like carbon, as a thin film of non-conducting material has a powerful influence on the electrical resistance of the gap between the discharging and collecting electrodes. Mechanical tapping, or compressed air, should be employed to remove the precipitate from the treater, either at long intervals by stopping the current, or at short intervals without stopping. A method of rendering the deposit electro-conductive by returning or adding a percentage of dust to the gases entering the precipitator has been patented by Huntington, Heberlein and Co. [20] A high efficiency in dealing with blast-furnace gases is not essential, but, as already pointed out, it is most essential in protecting platinum catalyst from poisoning.

An ingenious method connected with electrical separation is to pass the gases through vertical pipes, which serve as the receiving electrodes, and are suspended in groups of four placed close together and equidistant from a common centre. [21]

The subjects remaining to be dealt with under the head of plant and machinery include air purifying, emulsifying, expressing, extracting, fireproofing, grading, heat exchange, insulating, mixing, pumping, sampling, separating, storing. sublimation, etc, for all of which patents have been granted during the past year. A few items of interest will be selected.

A patent has been granted to J. W. Hinchley and G. Gorton [22] for an apparatus for expressing liquid from peat and other fibrous or carbonaceous materials. The material, after being heated by hot fluid which does not make direct contact. is pressed by two annular pistons. In a later patent by J. W. Hinchley [23] the pressed material is extruded from a cylindrical chamber by way of nozzles fitted with dies of such a size that the necessary pressure may be maintained within the chamber.

[19] *Chem. and Met. Eng.*, 1919, 20, 59; J., 1919, 163A.

[20] Eng. Pat. 127119; J., 1919, 52A.

[21] Huntington, Heberlein and Co., and H. C Bingham, Eng. Pat. 122534; J, 1919, 164A.

[22] Eng. Pat. 123774; J., 1919, 275A.

[23] Eng. Pat. 125672; J., 1919, 397A.

Liquid is previously expressed from the material by contact with plates of rigid porous material. An ingenious extractor which can also be used as a dyeing machine has been patented by British Dyes, Ltd., J. Turner, and T. P. K. Crosland.[24] It consists of a cylindrical vessel containing the liquid in the lower chamber, and the solid to be extracted on a tray fitted air-tight across the middle but communicating with the liquid by a number of passages closed by valves which operate automatically by the admission of air or steam. This provides for continuous extraction.

In the recovery of volatile solvents, H. J. Pooley and G. Scott and Son[25] have patented apparatus whereby the whole of the air or gas in a heated drying chamber is circulated rapidly by a large fan, and a small proportion is continuously removed by a small fan, passed through a recovery plant, reheated, and returned to the chamber. Heat is conveniently applied to the air or gas at a point in the suction pipe of the large fan.

A patent by the Wärme-Verwertungsges. m.b.H.[26] provides for the recovery of the heat of liquid slag, granulated by air, the heat being used to raise steam in a tubular heat exchanger.

There are two useful papers on heat insulation and lagging materials, one by J. S. F. Gard,[27] and one by R. Thomas.[28] Both authors agree that magnesia is the best insulator for retaining heat, though their figures do not agree well as to the comparative efficiencies of such materials as asbestos, slag wool, etc. One concludes that a covering of more than $1\frac{1}{2}$–2 inches is of little value, and that steam pipes of small diameter ($\frac{3}{4}$–1 inch) should be covered only with the best insulators.

Wire cloth is finding extended use in the chemical industry.[29] Heavier grades are replacing perforated metal as backings for strainers, centrifuges, filters, etc., having the advantage of greater air space. The finest cloth made in the United States is 250-mesh, but cloth as fine as 350–450-mesh has been made in Germany. Wire gauze of 200-mesh will retain the water from a mixture of water and light oil, and can be used in separating them. Both water and oil will pass through cloth of 180-mesh. The chief difficulty with wire cloth is keeping the openings uniform when it is bent or rolled. A patented design of spiral overlapping is said to get over this difficulty.

We welcome the development of " A New Prime Mover of high efficiency and British origin." [30] This refers to a new internal com-

[24] Eng. Pat. 123774 ; J., 1919, 275A

[25] Eng. Pat. 127909 ; J., 1919, 522A.

[26] Ger. Pat. 311639 ; J., 1919, 854A.

[27] Chem. Trade J., 1919, 64, 17 ; J., 1919, 97A.

[28] J., 1919, 357T.

[29] A. A. Campbell, J. Ind. Eng. Chem., 1919, 11, 761 ; J., 1919, 853A.

[30] F. E. D. Acland, J. Roy. Soc. Arts, 1919, 67 463 ;. J., 1919, 487A.

bustion engine, designed by W. J. Still, utilising either liquid or gaseous fuel in its main working cylinder. The cylinder wall is about one-third of the usual thickness. The cooling water of the jacket is allowed to rise considerably in temperature and generates steam. The exhaust gases are similarly employed for steam raising and also for preheating the water in the steam generator system. The steam thus generated is admitted on one side of the main piston, so that every other stroke is assisted by steam. The steam exhausts at a slight superheat, usually to a condenser. The chief advantages claimed for the Still engine are the following :— At normal loads the thermal efficiency is at least 25% more than that of any known internal combustion engine of similar proportions ; mechanical stresses are reduced ; the engine can be started readily against loads ; when using oil, the compression pressures necessary to ensure ignition can be reduced by 50% as compared with the Diesel system ; a thermal efficiency of 41% is possible as against $18\frac{1}{2}\%$ for the best steam turbine ; and additional steam gives a large range of overload.

FUEL.

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CHEMISTRY AND CONSTITUTION OF COAL.

WORK on this question is proceeding steadily in various quarters, and accumulation of facts and data is going on, though no new 'generalisations, that would throw much light on the problem, have been arrived at. W. A. Bone and R. J. Sarjant [1] have further examined the action of pyridine on coal, and find that the amount extracted is seriously affected by oxidation of the coal (either previously, or by the presence of oxygen during the extraction), or by water in the pyridine. A Durham coal extracted *in vacuo* yielded 32% to dry pyridine, whilst in presence of oxygen only 18% was extracted. On the other hand, the corresponding figures for a Barnsley hard coal of similar ultimate composition were 11·6% and 13·1%. The pyridine extract of the Durham coal gave 52% of its weight to chloroform ; but this chloroform extract was certainly not (as in Wheeler's view it should have been) a pure coal resin.

F. Fischer and H. Gröppel [2] heated coal for a while to 550°-600° C., then suddenly cooled it, and extracted in succession with petroleum spirit, benzene, and chloroform. Much more was extracted than from the raw coal, and the substances removed by the different solvents were very different. Their nature has not yet been ascertained : and they must, of course, be largely products of decomposition of the coal at the high temperature used.

Marie C. Stopes [3] has examined microscopically four separated portions of a banded coal from Hamstead colliery. These, provisionally called " fusain " (mother of coal or mineral charcoal), " durain " (dull and hard), " clarain " (bright), and " vitrain " (brilliant, conchoidal fracture), could be fairly well separated by hand, and showed differences in structure under the microscope, and in their effect on a photographic plate. F. V. Tideswell and R. V. Wheeler [4] examined chemically the

[1] *Proc. Roy. Soc.*, 1919, A **96**, 119 ; *J.*, 1919, 752A.
[2] *Ges Abhandl. zur Kenntniss der Kohle*, 1917, **1**, 68 ; *J.*, 1919, 400A.
[3] *Proc. Roy. Soc.*, 1919, B **90**, 470 ; *J.*, 1919, 452A.
[4] *Chem. Soc. Trans.*, 1919, **115**, 619 ; *J.*, 1919, 614A.

same four substances. Fusain they found to be different from the rest ; but vitrain. clarain, durain, in this order, showed diminishing moisture, increasing ash, and diminishing activity towards solvents and reagents. They all gave, when destructively distilled, similar products in different quantities ; and the authors conclude that each of them is composed of the same " reactive " and the same " inert " substances in different proportions, the ratios of reactive to inert substances in the three being in proportion to the numbers 10, 9, 7.

F. Fischer and his colleagues have worked at the action of various reagents on coal. Fischer and H. Niggemann [5] have extended to all types of coal the work on the action of ozone referred to in last year's Report. Black or brown, brittle, acid-reacting, hygroscopic substances were obtained, soluble in water or alcohol but only slightly in other neutral solvents, and decomposing at about $100°$ C. with evolution of carbon dioxide. The quantity increased as the coke-yield of the coal decreased. Anthracite gave 48% of its weight of these products and lost 86% ; evolution of carbon dioxide always occurred during ozonisation. Cellulose, graphite, coke, and charcoal did not yield similar products on ozonisation, and coals freed from bituminous constituents yielded as much as the raw coal. It is only, therefore the " humic " substances in coal that yield them. When heated these products decompose. and at $250°$ C. yield substances insoluble in water, but soluble in alkalis. F. Fischer and H. Tropsch [6] have endeavoured to determine the methoxyl group in coal, acting on the coal suspended in phenol, using pyridine to dissolve any methyl iodide ; in no true coals was any methoxyl group found, though lignites and peat gave methyl iodide corresponding to 1 2% of methoxyl. The same authors [7] have investigated the hydrogenation of coals by heating with hydriodic acid in presence of red phosphorus. Bitumen-like substances soluble in chloroform were obtained at $200°$ C , in amount rising from 12% of the coal in the case of anthracite to 70% in the case of a gas-coal or cannel. The acid wash-waters from the process contain ammonia and organic amino-compounds, and the nitrogen of the coal is completely removed. By heating gas-coal to $280°$ C. instead of $200°$ C , about 30% of a colourless liquid resembling petroleum was obtained. S. Hilpert, H. Keller, and R. Lepsius [8] give the results of treating coal with acetic anhydride and zinc chloride, and with a mixture of sulphuric and nitric acids ; and J. Marcusson [9] discusses the relationships and the behaviour towards various reagents of coal and of substances obtained from various

[5] *Ges. Abhandl. zur Kenntniss der Kohle*, 1917, 1, 30 ; *J.*, 1919, 39A.

[6] *Ibid.*, 1918, 2, 151 ; *J.*, 1919, 523A.

[7] *Ibid.*, 1918, 2, 154 ; *J.*, 1919, 855A.

[8] *Ibid.*, 1917, 1, 22 ; *J.* 1919, 399A.

[9] *Chem.-Zeit.*, 1918, 42, 437 ; *J.*, 1919, 98A.   *Z. angew. Chem.*, 1919, 32, 113 , *J.*, 1919, 350A.

natural asphalts, and classified as "asphaltenes," "carbenes," and "carboids"; but the many data thus obtained can only yet be looked on as material which can be useful for later generalisations. The last author also publishes work [10] on the humic acids produced from coal and lignite. He shows that these probably contain a furan nucleus, and are mixtures of nitrogenous and non-nitrogenous acids. He thinks that both the oxygenated and the nitrogenous constituents of coal are derived from humic acids.

WEATHERING -DETERIORATION -SPONTANEOUS COMBUSTION- STORAGE.

G. C. Jones [11] criticises Porter and Ovitz's conclusions, referred to last year, [12] on the ground that there is no evidence to show that the coal did not actually lose weight during the period of storage, and that hence the lowering of the calorific value is not necessarily a measure of the amount of deterioration through weathering. He shows from Porter and Ovitz's tables that the average ash rises from 6·8% at the beginning to 7·3% after a year and 8·4% after two years, and concludes that this is due to a corresponding loss of volatile substances from the coal. Porter in reply [13] points out that, though the large bulks of coal concerned were not weighed, yet direct experiments on similar coals had shown that they did not lose volatile matter during weathering; that most of the recorded work on the subject shows that actual increase of weight occurs, since there is absorption of oxygen and little or no evolution, at the ordinary temperature, of water vapour or of carbon oxides; and that the experimental errors in the sampling make any deductions based on the ash-content of little or no value.

These conclusions of Porter's are confirmed by the work of R. V. Wheeler, [14] who finds that the gases occluded in weathered coal and removed at 15° C. contain no oxides of carbon, but that at 100° C. oxygen, carbon monoxide, and carbon dioxide are all given off. When coal is artificially weathered by passing air over the finely divided coal, the amount of absorption (and of gases afterwards evolved into a vacuum at 100° C.) is greater when dry air than when moist air was used. The first absorption of oxygen by newly won coal is very rapid, but the rate soon sinks to a slow but long-continued absorption. Wheeler concludes that the oxygen forms an addition-compound or "complex" with some constituent of the coal, and that this complex begins to break down at 100° C., both oxides of carbon being products of its decomposition. (Compare Bone, mentioned in last year's Report, p. 22). J. R. Partington, however, [15] considers that the oxygen is merely adsorbed,

[10] *Z. angew. Chem.* 1918, **31**, 237; *J.*, 1919, 98A.
[11] *J.*, 1919, 58R. [12] *Ann. Repts.*, 1918, **3**, 21. [13] *J.*, 1919, 346R.
[14] *Chem. Soc. Trans.*, 1918, **113**, 945; *J.*, 1919, 65A.
[15] *Chem. News*, 1919, **118**, 50; *J.*, 1919, 125A.

and does not form any compound : he maintains that the rapid initial
rate, followed by slow and continuous absorption, and also the difference
between moist and dry air, are evidences of adsorption. He considers
that carbon monoxide is the direct product of oxidation of the
coal, but that the dioxide is formed only with the aid of moisture
$(CO + H_2O - CO_2 + H_2 :$ or $C + 2H_2O - CO_2 + 2H_2)$, when hydrogen
is also formed. To this Wheeler and F. V. Tideswell reply [16] that oxygen
circulated over duram at $100°$ C. took up no hydrogen ; that moist
mixtures of carbon monoxide and air similarly circulated formed no
hydrogen ; and that mixed hydrogen and air suffered neither loss nor
gain of hydrogen : whilst in all these experiments carbon monoxide and
dioxide were both formed. Further, the rate of absorption of oxygen
by coal increases as the temperature rises, whereas if it were an adsorp-
tive action the rate should decrease, as that of nitrogen actually does.

Wheeler, in the paper quoted above, describes experiments in which
finely divided coal contained in a glass tube was placed in an electrically
heated sandbath, and air drawn over it. As the temperature of the
bath was gradually raised, that of the coal rose correspondingly, so that
thermometers in the coal and in the bath showed a constant difference.
After a certain temperature was reached, however, the coal rose more
rapidly in temperature than the bath (owing, obviously, to chemical
action of the air on the coal), and the curves showing the march of the
temperatures of the two crossed. This crossing point was taken as the
" ignition temperature " of the coal The ignition temperatures of
thirty-two different coals varied from $165°$ $220°$ C, and were higher as
the oxygen-content of the coal was less.

The possibilities of spontaneous combustion and of explosion in the
case of pulverised coal are discussed in the report of the Fuel Research
Board ,more fully referred to later on (p. 27). With suitable arrange-
ments and careful working there is little or no danger from spontaneous
combustion . first, because the amount of pulverised fuel stored in one
place need never be more than about 24 hours' supply, and second,
because access of air to and exit of burnt gases from any part of the
bulk other than the outer surface are necessarily so slow. Instances
are quoted in which powdered coal has been stored in bulk for several
weeks without any change ; and others in which, though combustion
has occurred in the middle of the mass, it has been self-extinguished,
and has produced no result further than the caking of the central por-
tions. Naturally, care should be taken to have the storage bins out of
the range of sources of outside heat. The dangers of explosion from
mixtures of coal-dust and air, are minimised in modern plants in which
cleanliness is a feature; but even in older plants where this danger has
not been recognised, and where the whole installation has been thickly
covered with dust, no serious explosions or fires have occurred. In the

[16] *Chem Soc. Trans.*, 1919, **115.** 895 ; *J.*, 1919, 671A,

Holbeck system of distribution, a mixture of air and coal-dust constantly circulates through the mains ; but the proportion of air is much below that needed for complete combustion, and the speed of transport is so high that backward communication of flames from the burners is not possible.

COMBUSTION OF FUEL FOR POWER PURPOSES.

The Conference on Power Plant in Chemical Works, at the Annual Meeting of the Society, was, naturally, largely occupied with the question of the economical use of fuel. C. J. Goodwin [17] took up the subject of waste-heat boilers, and gave examples of economies realised or realisable by utilising the waste gases from lime-kilns, vertical gas-retorts, and the exhaust from gas-engines to raise steam in boilers. He pointed out that for success, the process must be carefully studied, and the type and dimensions of the boiler designed to suit : usually fire-tube boilers are to be preferred to water-tube boilers, as they do not allow leakage of air and consequent cooling of the gases. In a table, the author shows for coke-ovens, open-hearth steel furnaces, gas-works retorts, regenerative glass-furnaces, and gas-engines, the probable efficiency attainable in waste-heat boilers, and the reduction by this means in the percentage of the total calorific effect of the fuel lost. These reductions vary from the non-regenerative coke-oven, in which the reduction is from 81 to 11, to the much more efficient regenerative glass-furnace, in which a reduction from 24 to 9 is possible. On the whole, the efficiency of waste-heat boilers rises as the pressure of steam required from them is lower ; so that they are especially available for chemical works, in which a large amount of low-pressure steam is frequently required. In small gas-engine installations, where it would not be worth while to generate the small amount of steam that they could produce, the exhaust gases can often be economically utilised in heating water. A limit to the efficiency of waste-heat boilers lies in the fact that gases containing sulphur dioxide, when cooled to near the boiling-point of water, rapidly corrode tubes and fittings ; and the author draws attention to the new process of " calorising " almost any metal by the formation on its surface of an aluminium alloy, which is practically incorrodible in ordinary use. Discussion on the paper related largely to the question how far induced draught could be economically applied to boiler furnaces, as compared with chimney draught and its accompanying loss of heat in the chimney gases, and on the point raised by H. M. Ridge, whether economy would not in many cases be more successfully attained by endeavouring to utilise the heat of the waste gases in the process itself from which they were derived--for example, by using them to pre-heat air needed in the process--than by using them to raise steam.

[17] *J.*, 1919, 213т.

W. A. Bone and P. St. G. Kirke [18] gave an account of developments
and improvements in the Bonecourt surface combustion boiler. Two
recent types are described, in both of which the granular packing of the
fire-tubes is done away with. In the first, tubes 6 inches in diameter
are used, packed with rectangular bricks which will just enter the tube,
and which are arranged one behind the other so that opposite sides of
them form as it were two spiral staircases along which the gases pass.
In this way the boiler can be made longer, the gas can pass through at
a higher speed, the combustion is not concentrated into quite so short a
space, and a dust-free gas is not of such great importance as in the
original type. In the second recent type, the refractory material is
dispensed with, the tubes are only 2 inches in diameter, and an iron
spiral that will just pass into the tube is used as contact surface. The
spiral travel of the burnt gases produces the same result as the baffling
due to the packing in the original boiler, causing every portion of the
gas to impinge frequently upon the material of the tube and give up its
heat to it.

D. Brownlie, [19] in continuance of the work quoted in last year's
Report,[20] gives statistics in regard to 100 colliery steam-raising installa-
tions, comprising 570 boilers (500 Lancashire, 2 Cornish, 37 egg-ended,
and 31 tubular). The fuel used was extremely variable, the ash-
content ranging from 6·1 to 37·8%, with an average value of 15·5% ; the
average calorific value was 10,500 B.Th U. The author classifies the
coal supplies into 52% of high-grade coal, 32% of poorer but yet mer-
chantable coal, and 16% of what, but for its use at the colliery, would be
waste. The idea, therefore (supported by a statement in the report of
the Coal Conservation Committee), that collieries burn chiefly refuse and
unsaleable coal, is a complete fallacy. The same data are given in the
paper as in that of last year ; but it will be sufficient to quote the
averages of the fuel consumption, 18·9 lb. per sq. foot of grate area, the
percentage of carbon dioxide in the flue gases, 7·5, and the overall
efficiency, 55·5%. Only five of these installations had mechanical
stoking ; and their results were poorer than those yielded by hand-
stoking —probably because of the great variations in the quality of the
coal used from time to time. The author holds that the average
efficiency could be raised, easily, from 55 to 70%, by attention to the
tightness of the brickwork of the settings, by the introduction of
economisers and superheaters, by regulation of the draught, by treat-
ment of the feed-water, and by proper scientific supervision and control.
The same results as at present could be got if from 25 to 50% of the
boilers were shut down and the remainder worked at a higher efficiency.
The whole cost of the reorganisation could be saved in about 18 months.
Taking these installations to be representative of the colliery installa-

[18] J:, 1919, 228т.   [19] Engineering, 1919, 108, 101, 138.
Ann. Repts., 1918, 3, 24.

tions throughout the country, he estimates the resulting saving of coal
to b : 3·7 million tons, out of the 18·5 million tons now annually con-
sumed. By burning more waste (to an extent quite practicable under
existing circumstances), a further saving of $2\frac{3}{4}$ million tons could be
effected; and if modern methods of lagging steam-pipes were universally
adopted, and exhaust steam everywhere utilised in turbines, the saving
might be increased to 50% of the whole, or $9\frac{1}{4}$ million tons. The author
points out the immediate practicability and relatively small cost of
effecting these economies, as compared with the very problematical
saving of 13 million tons suggested by the Coal Conservation Committee
in their proposal for large electrical power stations, and the cost of
carrying out their scheme; and mentions especially in this connection,
the fact that some 15 million tons of coal are used in the generation of
steam for heating, boiling, and various chemical purposes, apart from
the generation of power.

P. Parrish, at the Power Plant Conference at the Society's Annual
Meeting, [21] read a paper on raising steam from low-grade fuel, in which
he records the results of burning coke-breeze, all passing a half-inch
mesh, and of which 25% passed a $\frac{1}{8}$-inch mesh, and which contained
17–28% of ash and 12–16% of moisture. Lancashire boilers were
used, with Crosthwaite forced draught air-tubes, the air being intro-
duced by an injector, and the secondary air supplied near the bridge of
the furnace, under the control of the chimney. The flue gas was
continuously tested for carbon dioxide, and constant care was necessary
in regulating the air-supply and in regularly cleaning the fires from
clinker. The removal of "drift" from the boiler flues every six weeks
was also necessary. Mixture of the breeze with broken coke so as to
make a more porous fuel bed did not make the boiler any more efficient;
but its ordinary working was effected at a very low cost. The figure
46·5d. represented the cost of raising steam, as compared with 59d. to
95d. in the published results of eight Government factories using coal.
But the author thought that coke breeze would be most efficiently
burnt outside of the boiler, in a type of producer. A modified step-
grate would be necessary, such that the clinker could be removed almost
automatically, and arrangement would have to be made for pre-heating
the breeze or other low-grade fuel.[22]

Another method of dealing with coke-breeze is adopted by Kayser [23]
who briquettes it with 5% of pitch and 1% of a liquid binder (tar), heats
it with superheated steam and presses it into ovoids. Addition to the
breeze of 20–25% of coal-dust gives a briquette more suitable for steam-
raising. A. Stober [24] also records experiments on the use of coke.

[21] J., 1919, 224т.   [22] Compare Ann. Repts., 1918, 3, 30,
[23] J. Gasbeleucht., 1918, 61, 541, 556; J., 1919, 34A.
[24] Stahl u. Eisen, 1919. 39, 525, 567; J., 1919, 482A.

Lump coke containing up to 50% of breeze had to be used, and was fed down a shaft upon the grates of water-tube boilers with chain-grate stokers, so as to be heated to ignition point before it reached the combustion chamber. Segregation in the bunkers led to irregular combustion, the rate of steaming only reached 50% of that with coal, the thermal efficiency was only 60%, and the cost of clinkering and attendance made the cost of steam greater than with coal. Hand stoking, with arrangements for primary and secondary air similar to these described by Parrish,[25] gave much better results, but the rate of steaming was still less than with coal, and only if the price of coke is more than correspondingly below that of coal is the cost of steam lower than when using coal.

No new work on the fusibility of coal-ash has appeared during the year; but W. A. Selvig, W. C. Ratliff, and A. C. Fieldner [26] summarise the results of previous work, and A. C Fieldner, A. E. Hall, and A. L. Feild [27] have published a most valuable monograph embodying not only the details of their own previously published work, but a history of the subject, and a very complete bibliography up to about 1916. The contents cannot be usefully summarised in the space here available, but the publication should be in the hands of all who are interested in the matter.

POWDERED COAL.

The subject of powdered coal firing has received attention at the hands of the Fuel Research Board, who publish [25] a report by L. C. Harvey on " Pulverised Coal Systems in America " In this elaborate report much detailed information is given, accompanied by drawings of plant, of the varied applications of powdered fuel, together with accounts of the experience of actual users. The general procedure is to crush the coal, remove accidental iron by passage over magnetic separators, dry the crushed coal by hot furnace gases, and feed it into pulverisers, whence, by means either of screens or of a current of air of regulated speed, the fine portions are separated and carried away to storage, whilst the coarser fragments fall back into the pulveriser. Air separation is said to yield a more uniform product, and is free from the liability to pass coarser particles which accidental damage to screens may allow; but screen separation produces a larger proportion of extremely fine powder. The pulverisation is usually carried to a minimum fineness in which 95% will pass a screen of 100, and 85% one of 200 meshes to the inch. Transportation of the pulverised coal is effected by one of three methods screw conveyors, compressed air, or

[25] Loc. cit.   [26] Chem. and Met. Eng., 1919, 20, 274; J., 1919, 349A.
[27] U.S. Bureau of Mines, Bull. 129; J., 1919 125A.
[25] Special Report No 1; J., 1919, 190R.

" air mixture." In the first two, the fuel is delivered into storage-bins
near the burners, and is thence carried to the burners either by screw-
conveyors or by air-pressure again ; in the third, the coal dust mixed
with about half the amount of air required for combustion is blown by
fans through a complete pipe-circuit, from which branch-pipes governed
by valves lead direct to each of the burners ; any excess of fuel beyond
that required by the branch-pipes is returned to the main storage-bin.
The burners are usually very simple, the coal-dust being blown through
a central nozzle by air-pressure, and inducing a secondary air supply
through a surrounding annulus. In the early forms too high air-pressure
was used, and the current carried away large quantities of ash. Now
that lower pressure is used, the gases remain long enough in the com-
bustion chamber to allow of settlement of the ash, most of which
collects as fused slag at the bottom of the chamber, and is easily re-
moved. Accounts of costs of several installations are given, from
which the general conclusion is drawn that, having regard to coal-saving
alone, and taking no account of collateral advantages, the installation
of a powdered coal system is economical if the cost of coal is 20s. per
ton or more. The question of storage has been already discussed earlier
in this report (p. 22).

A wide range of fuels is available for use in pulverised form.r The
best is, of course, a good bituminous coal high in volatile matter and
low in ash ; but generally it may be stated that any fuel with a fair
amount of volatile matter, even though its ash-content be very high,
can be burnt, and burnt completely. Accordingly, whilst anthracite
or coke is not very suitable, many low-grade coals with 30-40% of
ash, at present entirely wasted, can be economically used in the powdered
form ; and the capability of using such low-grade fuels is one of the great
merits of the system. Powdered fuel has been applied in America to
almost all kinds of metallurgical furnaces, to steam raising in both
Lancashire and water-tube boilers and also in locomotives, and on a
small scale for the central heating of buildings ; and a large and interest-
ing section of the Report is formed by the letters of users giving accounts
of the advantages and disadvantages attending its use.

Harvey's summary of the situation at the end of the report is highly
favourable to powdered coal as a fuel : he contends that it is more
efficient, in utilising a greater proportion of the total heat-value of the
fuel, than any other process, that consequently economies in fuel con-
sumption of from 20-50% can be effected by it, that almost any grade
of fuel, and especially low grades that would be otherwise waste, can
be utilised as powder, that it effects a great saving in labour, and that,
as the combustion is complete, its general adoption would greatly
reduce the smoke nuisance. Dealing with the ash presents no difficulties
save in a few special cases, and if plants are suitably designed there is no
danger of explosion or of spontaneous combustion.

In a paper read before the Iron and Steel Institute,[29] L. C. Harvey
gives further details of the application of powdered fuel to metallurgical
processes, especially those concerned with iron and steel. The paper is
chiefly concerned with the engineering details of installations, but in the
introduction he makes an interesting estimate of the saving realisable
by substituting powdered coal for the present modes of firing. Taking
the coal-consumption of 169 million tons as classified by the Coal
Conservation Committee in their first report, and estimating in each
class the proportion which probably could be used as powdered fuel, he
arrives at a total of 44·6 million tons. Were pulverised coal installed in
all these cases, 32·6 million tons would be sufficient for the work, effecting
a saving of 12 million tons of coal, or, at 30s. per ton, of £18,000,000.
The capital cost of the necessary plant would be £27,500,000
and the annual cost of working, including depreciation, £11,000,000 ;
so that the saving, £7,000,000 per annum, would clear off the capital
investment in less than four years. Accounts of the use of powdered
fuel in open-hearth furnaces and in puddling furnaces respectively are
also given by Harrison,[30] and by W. Simons.[31]

C. J. Goodwin, in the paper already quoted (p. 24), suggests the
application of powdered fuel in many furnace processes in chemical
works, and also proposes a combination of powdered coal fired high-
pressure boiler with waste-heat boiler for those works in which steam
is used not only for power but also for evaporation, heating, etc.

" COLLOIDAL FUEL."

The great mobility of powdered dried coal allows it to be transported
through pipes and conduits almost like a liquid ; and if it be suspended
in a liquid like fuel oil, it can be passed through an ordinary fuel oil
burner, and thus utilised in any oil-burning installation without altera-
tion of the plant. The difficulty in utilising such a mixture lies in the
fact that on storage the solid separates from the liquid by gravitation.
This difficulty has been overcome by the Submarine Defense Associa-
tion of New York, whose secretary, L. W. Bates, has published several
reports in pamphlet form,[32] the method consisting in the use of a
substance called a " fixateur," the nature of which is at present secret.
The addition of 1% of a fixateur to a mixture of 60 70% of oil and
10–30% of coal-dust forms a sort of colloid suspension which remains
homogeneous for long periods. The advantages of this form of fuel
(which was developed for naval use, and has as yet hardly been tried
outside of the U.S. naval experiments), beyond the fact mentioned
above, are that it economises oil, and provides (when high-class coal is

[29] J. Iron and Steel Inst., 1919, 99, 47 ; J., 1919, 349A.
[30] Engineering, 1919, 108, 45.
[31] Iron and Steel Inst., Sept., 1919 ; J., 1919, 771A.
[32] J., 1919, 165R, 349A, 752A.

used) a fuel of even higher calorific value per unit volume than the original oil. Further, coal-tar can be mixed in the fuel in considerable proportions. Two typical fuels, known as Grade 13 and Grade 14, have the following compositions :- -

	Grade 13.	Grade 14.
Coal	30	30
Coal-tar, etc.	—	12
Fixateur . . .	1·5	1·3
Mexican reduced oil . . .	28·8	—
Texas Navy oil	8·5	6·8
Pressure still oil	31·2	50·0
	100·0	100·0

Another advantage, having regard to the prospective use of colloidal fuel for industrial purposes, is that solid fuels which cannot be used (or cannot be advantageously used) alone in powdered form, such as coke, or anthracite very low in volatile matters, can be burnt quite well in colloidal fuel, even when their ash-content is very high ; so that the range of usable low-class fuels is further extended.

LIQUID FUEL.

Boring for oil was started,[33] under the auspices of the Government, in Derbyshire in the autumn of 1918 ; and oil was struck in May, 1919, at Hardstoft, at a depth just over 3000 feet. It is a petroleum oil containing naphthenes, and the early samples furnished about 7% of motor spirit, 40% of burning oil, 20% of gas oil, 30% of lubricating oil, and 3% of solid paraffin. The oil has continued to flow at the rate of some 400 gallons per day, but no further developments of any great importance have taken place, and we are still dependent for liquid fuel, as far as our internal resources are contained, upon the products of distillation of oil-shales and of coal.

The availability of alcohol as fuel for internal combustion engines has formed the subject of inquiry for an Inter-Departmental Committee, which was appointed in October 1918, and reported in June 1919.[34] The Committee do not look for any profitable large-scale production of power-alcohol from vegetable sources in Britain, but think there is scope for such production in tropical and sub-tropical parts of the Empire. They have discussed the possibility of converting into alcohol the ethylene in gas produced in gas works and coke-ovens, but consider that large-scale experimental work is needed before its economic success or otherwise can be demonstrated. They have instituted two researches, one scientific, under Prof. H. B. Dixon, to accumulate data in regard to the combustion of alcohol and alcohol mixtures, and the other industrial, in the daily running for a period of six months of a

fleet of motor omnibuses fed with such mixtures. They further make several recommendations towards lessening the cost of denaturing, and removing restrictions from and providing facilities for the transport, storage, and distribution of denatured power-alcohol ; and they regard State experimental work, and State supervision and, if necessary, regulation of the industry, as desirable.

Valuable experimental work on the extraction of ethylene from coke-oven gas has been done at the works of the Skinningrove Iron Co., and an account of this was given to the Cleveland Institution of Engineers by E. Bury.[35] The gas was deprived of hydrogen sulphide, dried by passage through sulphuric acid, and the ethylene absorbed : in the first place by charcoal, from which it was then expelled by heat, but afterwards (and, it was found, much more economically) by strong (98%) sulphuric acid at 60° 80° C ; this rapidly removes 70 80% of the total ethylene present. The ethylsulphuric acid formed is decomposed by superheated steam, and a 70% yield of alcohol is obtained, whilst the acid is reduced in strength to 74% and is concentrated to 95% to enter the process again. A certain amount of destruction of the acid occurs, by reaction with impurities in the gas, but the sulphur dioxide so produced is made to react with hydrogen sulphide in the crude gas, and the resulting sulphur mist is filtered out by the oxide purifiers in which the excess hydrogen sulphide is destroyed, and all the sulphur so obtained is converted into sulphuric acid. The utilisation of all waste heat is effected as far as practicable in the process ; and though the work has not yet gone far enough to present accounts of costs and yields, the experimenters are confident that the process will work out to a commercial success. Should this be so, and should its adoption become general, the gas works and coke-ovens throughout the country could produce about 50 million gallons of alcohol yearly—a very sensible addition to the liquid fuel resources of the country.

Diesel engine fuel has received attention both here and abroad. K. Neumann[36] has worked at the vapour pressure curves of various oils, and the nature of the gas yielded at different temperatures, pressures, and periods of decomposition. Speed of vaporisation is greater as the specific gravity and latent heat of evaporation are smaller and the maximum vapour pressure is greater Rapidity of evaporation is desirable, but not at too low a temperature. lest air should be displaced by the vapour, and too little be left in the mixture ; thus oils with high vapour pressure at low temperatures are not suitable. Fine atomisation of the injected oil facilitates evaporation. The relative rates of formation of oil-gas from paraffin oil, heavy coal-tar oil, and anthracene oil are given as 10 : 2 : 1.

[35] *Iron and Coal Trades Review,* Dec. 19 and 26, 1919 ; see *J.*, 1920, 94A.
[36] *Z. Ver. deuts. Ing.*, 1918, **62**, 706, 722, 763 : *J* , 1919, 452A.

structurally were found to be, when working with petrol, 100 ; with town gas (450 B.Th.U.) 91 ; with producer-gas containing a little water-gas (210 B.Th.U.) 87 ; with suction producer-gas (140 B.Th.U.) 82. The weight of a suction producer for a 30 b.h.p. engine was found to be 220 lb., and the fuel cost (with coke 45s., anthracite 55s. per ton) equivalent to petrol at 5s. 4d. per gallon. Suction gas would be a suitable alternative fuel for alcohol-motors. The Committee consider that the use of liquefied combustible gases is not practicable ; but with calcium carbide costing not more than £5 per ton, acetylene should be useful and commercially possible for enriching suction gas, and the similar application of naphthalene should be tried experimentally.

Several papers on the mechanism of combustion in gases have appeared during the year. H. F. Coward, C. W. Carpenter, and W. Payman,[19] have determined the lower limits of inflammability of mixtures with air of methane, hydrogen, and carbon monoxide, separately and together. The results show that for any of these mixtures Le Chatelier's formula holds, viz., if, n_1, n_2, etc. be the percentages of the various gases in a mixture at its lower limit, and if N_1, N_2, etc. be the lower limit percentages for each gas separately in admixture with air,

$$n_1 /N_1 + n_2 /N_2 + \text{etc.} = 1.$$

Upper limits were also determined for methane, hydrogen, and carbon dioxide, at 15·4%, 74·2%, 74·2% respectively, with air saturated with moisture at 18°-19° C ; and the examination of mixtures of two or more of these gases with air showed that the limits actually found agreed with those calculated from the formula as above.

W. Payman and R. V. Wheeler,[50] continuing their work on the propagation of flame in tubes,[51] have extended it to hydrogen, coal-gas, and a methane-hydrogen mixture. They find that Le Chatelier's formula is applicable to the calculation not only of limit-mixtures, but to propagation-speeds, in mixtures of two or more inflammable gases with air. Their results show that coal-gas is not suitable to use for testing miners' safety lamps, for even with "straight" or normal coal-gas the speed of propagation of flame attainable is more than double that attainable in methane and air mixtures, and the variations in the composition of coal-gas, especially the differences between "straight" coal-gas and a gas containing admixed water-gas, involve very great variations in the speed of travel of flame through them. Further, the ability of flame to pass through small holes or tubes appears to be to some extent a quality of the individual gas, besides its dependence on the speed of propagation, and to be possessed by hydrogen, and

49 Chem. Soc. Trans., 1919, 115, 27 ; J., 1919, 126A.
50 Chem Soc. Trans., 1919, 115, 36 ; J., 1919, 126A.
51 Ann. Repts., 1918, 3, 35.

conferred on mixtures containing it, in much higher degree than by methane.

R. V. Wheeler [52] has investigated the conditions of inflammation of mixtures of ethane and air in the same apparatus as he used for methane-air mixtures [53]; he has also investigated the effect, on the propagation of explosion, of turbulence produced by a rapidly rotating fan in the vessel. Flame is not so readily propagated in a turbulent mixture, no doubt because of the more rapid removal and wider distribution of the heat of the ignited portion. If it does spread, however, it travels much more rapidly than when the mixture is at rest. The action is probably altogether mechanical. The time-pressure curves with ethane and air are similar to those with methane and air. The mixture for complete combustion contains 5·63% of ethane, but those producing the highest pressure and the highest speed of propagation contain 6·5–7·0%.

W. Payman has studied [54] the propagation of flame in complex gaseous mixtures. From the nature of limit-mixtures, he deduces the generalisation that all mixtures, in any proportions, of lower-limit mixtures or of upper-limit mixtures, will remain lower-limit or upper-limit mixtures respectively. This, if the atmosphere be of constant composition for all, reduces to Le Chatelier's formula ; but the generalisation applies (though not the formula), whether the atmosphere in the several limit mixtures be alike or not. The effect, on the composition of the limit mixture, of change in the oxygen-content of the atmosphere was studied with methane as the combustible gas. As the oxygen-content rose from 13·7% to 100%, the percentage of methane fell, in the lower-limit mixture, from 6·4 to 5·7, and rose, in the upper-limit mixture, from 6·9 to 59·2. Differences from the results of Parker [55] (who used central ignition in a sphere) were found to be due to the position of the point of ignition ; for experiments with the tube arranged so that the propagation took place in different directions gave different results.

| Mode of propagation | Percentage of inflammable gas in lower-limit mixture. | | |
	Hydrogen. (with air)	Methane. (with air)	(with oxygen)
Upward	4·2	5·5	5·4
Horizontal	6·2	5·9	5·8
Downward	9·7	6·1	6·3
Central ignition	9·2	5·8	6·0

The speed of propagation in lower-limit mixtures of methane with variable atmosphere showed but little variation, rising from 21·9 cm. per

[52] Chem. Soc. Trans., 1919, 115, 81 ; J., 1919, 127A.
[53] Ann. Repts., 1918, 3, 35.
[54] Chem. Soc. Trans., 1919, 115, 1436, 1446, 1474 ; J., 1920, 94A, 95A.
[55] Chem. Soc. Trans., 1914, 105, 1002.

second for 13·7% of oxygen in the atmosphere, to 23·3 for air, then
falling to 19·9 for pure oxygen. The upper-limit speed was close to
19·0 for all mixtures. Further, the speed in both lower-limit and upper-
limit mixtures with variable atmosphere, using paraffin hydrocarbons
up to pentane, and mixtures of them, and also using carbon monoxide,
was so nearly the same, that it may be stated as approximately true
that the " limit-speed " has a constant value for all mixtures. To this
generalisation hydrogen appears to be an exception.

Examination of the speeds of propagation of other than limit-mix-
tures, showed in the case of mixtures of the first five paraffins with air
that the maximum speed was for all save methane (which was 67)
close to 82 cm. per second ; and mixtures of a pentane mixture and
a methane mixture having separately the same speed, say 40 or 60 cm.
per second, had the same speed as their constituent mixtures. This is
not true where the speeds are close to the maxima, nor where the
mixtures contain considerable percentages of an inert gas. The
maximum speed of a mixture of maximum-speed mixtures may be
approximately calculated from the assumption (justified by experiment
in several cases) that the resulting maximum speed is proportional to
the amount of each mixture present and to its maximum speed, or

$$S = \frac{aS_a + bS_b + cS_c + \cdot \cdot \cdot}{a + b + c + \cdot \cdot}$$

where a, b, c, are the percentages, S_a, S_b, S_c, the maximum speeds, of
the constituent mixtures, S the maximum speed of the resultant mixture.

In the third part of the paper the speeds of flame-propagation in
mixtures of carbon monoxide and air were determined, the maximum
(about 60 cm. per second) occurring with mixtures containing 45–50%
of monoxide. The speed with all carbon monoxide mixtures, however,
is greatly affected by the hygrometric state of the gas, increasing
rapidly as the amount of water vapour increases. The speeds of hydro-
gen-mixtures were also determined, of mixtures of air with methane
and hydrogen ($CH_4 + H_2$, $3CH_4 + H_2$), carbon monoxide and hydrogen
($CO + H_2$, $2CO + H_2$), carbon monoxide and methane ($CH_4 + CO$),
methane, carbon monoxide, and hydrogen ($CH_4 + CO + H_2$). The
effect of hydrogen or methane on carbon monoxide appears to be
similar to that of water vapour ; for the curve of speeds for carbon
monoxide, calculated from one of the mixtures ($3CO + H_2$), shows
uniformly higher values than those actually obtained with carbon
monoxide saturated with water vapour at 12°, but values for the other
monoxide mixtures, calculated from the " effective " curve, agree well
with experiment. All the other mixtures gave speeds in close agreement
with those calculated from their constituents. The same applies to a
set of figures obtained from mixtures of coal-gas with air ; but in the
case of producer-gas the discrepancies were very considerable, no doubt

because of the high percentage of inert substances in the producer gas.

It is interesting to note that in all these cases the mixture giving maximum speed contains more of the inflammable gas (in the case of carbon monoxide much more) than the mixture for complete combustion, as was found by Wheeler to be the case for the mixture giving the maximum pressure on explosion.

LOW TEMPERATURE DISTILLATION.

Not much work has been published during the year on the low-temperature distillation of coal. F. D. Marshall [56] has set out in general terms the amounts and qualities of the various products which a ton of average coal may be expected to yield by low temperature carbonisation, with or without gasification of the coke ; and S. W. Parr [57] has discussed the desirability of treating all coal by some such process, and of separating the sulphur-containing volatile products by fractional distillation from those containing no sulphur. F. Fischer and W. Gluud [58] have suggested a retort, rotating round a hollow axis plugged in the middle, through one end of which steam is admitted to carry off the volatile products through the other end ; and in a further paper [59] describe the liquid products obtained by its use. They found that the most volatile portions (b.pt. 20°–60° C.) were paraffins, those with b.pt. 60°–100° C were chiefly naphthenes, with paraffin admixture, and the higher members a more complex mixture, containing probably some aromatic compounds. F. Fischer and K. Keller [60] also examined the results of distilling coal in hydrogen at high temperatures and pressures, and found that as the temperature and pressure rose the yield of coke lessened, whilst those of volatile hydrocarbons and of tar increased. After tar ceased to come over, volatile hydrocarbons still continued to be formed, at the expense, of course, of the coke.

Besides the retort suggested by Fischer and Gluud (supra), two other forms of retort presenting novel features have been described, one by G. T. Beilby, [61] the other by F. A. Anderson, M. Deacon, and N. P. W. Brady. [62] In the first, material is fed by a hopper in a thin layer upon trays carried on a rotating table, and emptied by tipping at one part of their travel, the whole being contained in a gas-tight metal casing heated in a furnace and provided with appropriate outlets for the volatile products and for the coke tipped from the trays. The speed of travel is so arranged that the contents of each tray are completely carbonised in less than a revolution. In the second, the coal falls from

[56] *Gas J.*, 1919, **145**, 383, 451; *J.*, 1919, 212A.
[57] Western Soc. of Eng., U.S.A. ; *J.*, 1919, 212A.
[58] *Ber.*, 1919, **52**, 1035 ; *J.*, 1919, 563A.
[59] *Ber.*, 1919, **52**, 1053 ; *J.*, 1919, 564A.
[60] *Ges. Abhandl. zur Kenntniss der Kohle*, 1917, **1**, 148 ; *J.*, 1919, 526A.
[61] Eng. Pat. 124039 ; *J.*, 1919, 353A.
[62] Eng. Pat. 132744 ; *J.*, 1919, 810A.

a hopper at one end of the furnace upon a continuous belt conveyor,
which discharges the coke down an incline at the other end, and returns
beneath the furnace through two liquid seals. The furnace is heated
by zig-zag flues below the conveyor, and the roof is arranged to form
three or four inverted pockets, from the top of each of, which leads an
exit pipe controlled by a small exhaust fan, so that volatile distillation
products from successive stages of carbonisation can be separately
removed.

FUEL ECONOMY.

There has been a considerable output during the year of publications
on fuel economy and the better utilisation of various forms of fuel. A
very interesting paper, though its object is rather to enumerate and
state instances in which economy of fuel seems desirable and possible
than to suggest solutions of the problems raised, was read by R. F.
Bacon and W. A. Hamor before the New York Section of the Society.[63]
The paper itself should be read, though attention may usefully be
drawn to the account of attempts to separate the combustible portions
left in ordinary coal washery work, by flotation (which the authors
find practicable but too costly), and by re-washing (which has yielded
quite encouraging results), and also to the recommendation, in view of
the gradual diminution of petroleum supplies, that full and systematic,
investigation should be made of the oil-shale deposits of Colorado and
Utah.

The British Association Fuel Economy Committee made a report to
the September meeting of the Iron and Steel Institute,[64] in which they
express the view that great room for economy still exists in the practice
of British iron and steel works. The concentration on one site of
coke-ovens, blast-furnaces, steelworks, and rolling mills ; the thorough
(preferably electrostatic) cleaning of blast-furnace gases, and their
use, along with surplus coke-oven gas, in gas-engines rather than in
raising steam for power, the careful utilisation of the heat of the waste
gases from open-hearth furnaces, soaking-pits, stoves, etc., and the
recovery of the waste heat from molten slag, are the directions in which
economies are chiefly to be looked for ; but the Committee point out
that all these economies are dependent, not on the discovery of new
principles, but on thorough organisation and a system of thorough
scientific control, in the hands of members of the staff who are properly
trained fuel experts.

The same Committee also reported to the meeting of the British
Association at Bournemouth ; but their report is chiefly a résumé of
work done before the Committee's work was interrupted by the proposal
to merge their individuality in the Fuel Research Board, and a state-
ment of the directions in which work is now being undertaken. They

⁶¹ J., 1919, 161T.   ⁶⁴ J., 1919, 355A.

utter a warning to the Fuel Research Board, against the over-centralisa-
tion of work on this vast subject, and urge that the help should be sought
of workers all over the country who are properly equipped for research.

The " super-power-stations " proposals of the Coal Conservation
Committee,[65] have given rise to several critical publications, amongst
which the two most important are that of J. W. Cobb,[66] and that of
D. Clerk.[67] Cobb points out that the proposals of the Power Genera-
tion Sub-Committee of the Coal Conservation Committee involve the
use of electrical energy as the medium of transmission of the energy of
coal for the whole of the heating, lighting, and power purposes of the
nation. In regard to power, the Committee's own estimate of $1\frac{1}{4}$ lb. of
coal per h.p. hour implies that only 13% of the total calorific energy of
the coal is obtainable as electric energy at the generating station, and
distribution and transmission losses have to fall upon this 13%. Gas
engines have an efficiency of 25-30%, and the Metallurgical Sub-
Committee are found recommending the use in individual iron and steel
works of the blast-furnace and coke-oven gases, in gas-engines, as
sources of the power needed in the works for blowing engines, rolling-
mills, etc., instead of using them under boilers to generate electric
current to feed the general system, as the Power Generation Sub-Com-
mittee desire. In regard to heating, domestic and otherwise, far
higher efficiencies are obtainable by the use of gas and the other pro-
ducts of coal-distillation than are obtainable electrically. Even the
much abused open coal-fire, with all its secondary objectionable fea-
tures, ... es for a given heating effect only about half as much coal as is
needed to produce the same heating effect by electric radiators. The
efficiency of gas-works products, from the heating point of view, will
be still further heightened if the coke is converted into water-gas, and
the whole of the gaseous products are distributed through the mains.
In this way 50% of the energy of the coal could be delivered to the
consumer ; so that, gas being at least twice as efficient as coal for
domestic heating purposes, the 35 million tons of coal now used annually
for domestic heating would, if carbonised at gas works, provide all the
heating that it does at present and yield additionally all of the liquid
products of its distillation. What is true of domestic heating is also
true of industrial heating, save in the case of certain processes demand-
ing the use of very high temperatures ; in these processes there is a
field for electric heating in which it has no rival, and the question of
original coal-economy does not enter.

Clerk [67] enters into elaborate calculations of efficiency, from the
most trustworthy figures available for both gas and electricity. In
average gas-works practice there is obtainable from the gas 25, and
from the tar and coke 46, out of every 100 units of heat in the original

[65] *Ann. Repts.*, 1918, 3, 38.   [66] *Edinburgh Review,* Jan., 1919.
[67] *J. Roy. Soc. Arts,* 1919, 67, 337.

coal. If the gas be debited with the whole of the 89 units used in the process, its efficiency is 25/54 or 46%. In average electric-station practice (3·47 lb. of coal of 11,600 B.Th.U. per unit, according to Mr. D. Wilson, technical adviser to the Coal Controller) the efficiency is 8·5% ; so that gas is 5·4 times as efficient as electric current, in regard to the coal required to supply a given amount of energy. If the efficiency of appliances in which the energy is to be used be now considered, the ratio for heating, boiling, baking, furnace-work, etc., becomes about 4 ; for lighting, comparing 1-watt lamps and inverted incandescence burners, very nearly 1 ; and for power, comparing gas-engines and electric motors, 1·6. If instead of average practice, the best recorded practice in both gas-works and electrical station practice be taken, these figures become 3·24 instead of 4, 0·53 (½-watt lamps) instead of 1, and 1·3 instead of 1·6. The future efficiency suggested in the Coal Conservation Committee's Report (1 lb. of coal per h.p. hour) is 1·5 times as high as the best present practice, 2·3 times as high as the present average. Comparing electric current at this efficiency with coal-gas at the efficiency attainable by converting the whole of the coke into water-gas, the ratios would be, for heating 3·8, for lighting 0·77, for power 1·1 ; so that under all circumstances it is only lighting that shows advantage in point of economy for electrical working. It is estimated that the percentages of the total coal-gas used in the kingdom for these three purposes of heat, light, and power are roughly 55, 35, and 10, and on this basis calculation shows that were electricity substituted for gas in all these services, then for 100 tons of coal now consumed at the gas works there would have to be consumed at the central stations 265 tons, on the basis of the figures for average working, or 192 tons, on the basis of those for future working, given above.

Both of these papers will well repay detailed and careful perusal ; and taken in conjunction with such remarks as those of Brownlie (ante, p. 25) show that very careful consideration, and the compilation of accurate statistical information as to the efficiencies of present power-installations and the possibilities of their improvement, ought to precede any large-scale action that would be irrevocable, and that might tend to hinder, by its very magnitude, the march of further improvement.

GAS—DESTRUCTIVE DISTILLATION—TAR PRODUCTS.

By E. V. Evans, O.B.E., F.I.C.,

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Reconstruction in the gas industry is being pursued as expeditiously as the existing conditions allow, but progress is necessarily slow, for not only do such factors as the shortage of material, the attitude of labour, and the unfortunate financial status of the industry hinder reorganisation, but the lines along which progress shall be made remain not only debatable but in certain cases obscure. The ultimate factor determining the policy to be adopted must be that of fuel conservation, and this involves the more efficient utilisation of the raw coal now used for household purposes, the employment in industry of a larger proportion of the poor coal now wasted, and the operation of only the most efficient processes involving the use of coal. It is hardly to be expected that solutions to such comprehensive questions will be received with general concord in the industry, and the position is complicated by the fact that considerable research remains to be carried out before the gas chemist acquires a clear conception of the constitution of coal and its behaviour during destructive distillation. There is no doubt, however, that steady progress is being made and that a solid foundation is being built which will allow for extensive developments in the future.

CARBONISATION OF COAL.

Large-scale Carbonisation.

As regards the large-scale carbonisation of coal in horizontal retorts at high temperatures, there is a general tendency to increase the weight of coal carbonised in unit time with results which on the whole are beneficial. The recent work of many investigators, however, is in the direction of steaming the charge of coal with the object of producing results comparable to those obtained from the steaming of coal in vertical retorts. For this purpose special appliances have been devised for superheating the steam and distributing it in the heated mass of coal. E. Goffin [1] claims to have obtained per ton of coal carbonised, 19,000 cub. ft. of gas of a calorific value of 460 B Th.U. per cubic foot, representing 8·7 million B.Th.U. per ton of coal treated. He

[1] *J. Gasbeleucht.*, 1919, **62**, 253 : *J.*, 1919, 523A.

states that whilst the reduction in yield of coke was relatively small, an improved recovery of tar and ammonia was achieved.   R. J. Rew [2] who has secured the most successful results by steaming the coal charge in stop-ended retorts, attributes failures to (1) the use of wet instead of superheated steam, (2) the use of excess of steam, (3) the loss of time contact in the mass by using steam at too high a pressure, (4) the passage of steam over the coke rather than through it and the consequent scavenging of the retort rather than the coke.   He enumerates the advantages arising from short-period steaming and records results indicating the improved yields arising from carbonisation under such conditions.   In spite, however, of the many results which have been reported during the year from various sources, the practice of steaming the charge in horizontal retorts cannot be considered a proven process.

Progress is recorded in respect of the yields obtainable from vertical-retort systems of carbonisation.   At Uddingston L. Hislop [3] by steaming the charge of coal has obtained as much as 50,000 cub. ft. of 350 B.Th.U. gas per ton of coal carbonised, representing a yield of 17·5 million B.Th.U. in the form of gas which amounted to about 57% of the total calorific value of the original coal.   The yield of ammonia expressed as sulphate was 70 80 lb. per ton of coal treated and the gas obtained contained not more than 12% of inert constituents.   These results were obtained in a vertical retort installation of standard design, but could not be sustained for more than a day or two at a time owing to the impossibility of maintaining the required temperatures— particularly in the lower sections of the retorts.   The importance of temperature in the zone of maximum decomposition is exemplified by the work of L. J. Willien [4] who studied the degree of interaction between steam and carbon at increasing temperatures.

The following table shows the effect of temperature in the water gas reaction :— -

Temp , ° F.	Steam decomposed %.	Composition of gas by volume.		
		H_2	CO	CO_2.
1240	8·8	65·2	4·9	29·8
1400	25·2	65·2	7·8	27·0
1540	41·0	61·9	15·1	22·9
1750	70·2	53·3	39·3	6·8
1770	94·0	48·8	49·7	1·5
1960	99·4	50·9	48·5	0·6

[2] Gas J., 1919, 147, 557 ; J., 1919, 707A.   [3] Gas J., 1919. 146, 89, 607,
[4] Gas J., 1919, 146, 97 ; J., 1919, 314A.

The Gas Investigation Committee of the Institution of Gas Engineers has further investigated the conditions and yields at Uddingston. The Committee found that by steaming a charge of Lanarkshire coal 30,000 cub. ft. of gas of 385–394 B.Th.U. per cubic foot (after benzol extraction) could be obtained per ton of coal carbonised. The gas contained on an average 1·2 grains of naphthalene and less than 7 grains of sulphur compounds (other than hydrogen sulphide) per 100 cubic feet. The specific gravity of the gas was 0·500 and an average analysis showed : CO_2, 6·1% ; O_2, 0·3% ; C_nH_m, 1% ; CO, 23·9% ; H_2, 50·1% ; CH_4, 12·2% ; N_2, 6·4%. From this analysis the total inert constituents are shown to be 12·8%. Whilst the yields of tar and ammonia by this process were increased over normal working, only 6 cwt. of coke was made for sale per ton of coal carbonised, representing a reduction of about 23%. In general gas-works practice the quantity of coke produced for sale is approximately 10·5 cwt. per ton of coal and its ash content is about 17%. Hence the reduction of this yield to 6 cwt. which results from steaming the charge, must necessarily increase the ash content to about 30%, which is a serious drawback. The way out of this difficulty is suggested by Hislop himself, who favours complete gasification in vertical retorts suitably lengthened and heated. The economics of steaming in vertical retorts forms the subject of many contributions to the literature of gas manufacture in this and other countries. The relative merits of steaming in vertical or horizontal retorts to produce water gas at the expense of the coke, as compared with steaming so as to gasify a small proportion of the coke for the production of a gas which shall facilitate the process of carbonisation, have yet to be established. Insufficient attention appears to be given by investigators to the subject of the increased cost of purifying, storing, and distributing a gas of low as compared with high calorific power, and the sale of gas upon its calorific basis may appreciably modify certain conclusions already accepted by the gas industry.

Complete Gasification.

As regards the complete gasification of coal, it is of considerable interest to note the construction and apparent successful operation of three 50,000 cub. ft. per hour units of Dellwik-Fleischer's tri-gas system [5] at Vienna. E. Dolensky and A. Pott [6] state that these units, unlike those of the former plant, are constructed with revolving grates and that poor coal and lignites as well as the best gas coal may be handled with equal ease. A poor coal gasified at medium temperatures yields 65,000 cub. ft. of 320–340 B.Th.U. gas per ton of coal, the gas having the following composition : CO_2, 13·3% ; O_2, 0·4% ; CO, 23·9% ; CH_4, 5·5% ; H_2, 51·15% ; N_2, 5·1%. The total of the inert constituents

[5] Gas J., 1917, 139, 67.
[6] J. Gasbeleucht., 1919, 62, 261, J., 1919, 523A.

of this gas is 18·8%. Under the most favourable gas-making conditions, that is with good quality coal and at high temperatures, a similar volume of gas is obtained at the expense of the tar and oil products ; the calorific power of the gas in this case being approximately 430 B.Th.U. per cubic foot. The normal tar from this process is of port-wine colour by transmitted light, free from naphthalene, of sp. gr. 1·04 at 15° C., and is completely soluble in benzene. It contains 35–40% of phenols and resins, and yields on vacuum distillation 26–27% of fuel and lubricating oils. The yield of ammonia by this process is high, 90% of the nitrogen of the coal being recovered.

Owing to the shortage of coal—particularly on the continent—attention has again been directed to the carbonisation of lignites, peat, and wood,[7] and in this respect mention should be made of the work of K. Bunte[8] upon many kinds of lignite.

The results of gas-making tests with "Totis" Hungarian lignite containing 3·70% of sulphur show a yield of about 12,000 cub. ft. of 574 B.Th.U. gas per ton of air-dried lignite. The yields of tar and ammonia present considerable interest although the coke left in the retort is a grey, pulverulent mass of inferior quality which would require forced draught for its combustion. The gas, owing to its high sulphur content—82·5 grains of sulphur per 100 cub. ft. of gas, after lime-purification—is unsuitable for use, but it is suggested that other kinds of lignite containing less sulphur might prove more satisfactory.

Lignites have also been carbonised in low temperature plants such as the Del Monte, and in this case the residue from the retort is briquetted by the use of pitch, with apparently good results.

The carbonisation of coal dust has formed the subject of a patent by J. H. Corthesy and S. T. S. Castelli.[9] A generating chamber is divided into an upper and lower section ; coal dust is introduced into the upper section and is distilled by heat radiated from a centrally placed cone through which power gas generated in the lower section is conducted. · As the heat is insufficient for complete carbonisation a portion of the hot gases is returned into the upper section of the chamber by means of a fan and this maintains the coal dust in agitation. Only a crude separation is made between the upper and lower section, and the carbonised fuel gravitates into the lower chamber through the annular space left around the centrally placed cone. To the hot coke in the lower chamber air or air and steam is introduced, whereby a mixture of producer and water gases is made, and, as before mentioned, rises within the central cone. The two gases, namely illuminating gas

[7] E. Stansfield and R. E. Gilmore, *Trans.' Roy. Soc. Canada*, **11**, iii, 85 ; **12**, iii, 121 ; *J.*, 1919, 67A, 491A. E. Heuser and C. Skiöldebrand, *Z. angew. Chem.*, 1919, **32**, 41 ; *J.*, 1919, 215A.

[8] *J. Gasbeleucht.*, 1919, **62**, 34 ; *J.*, 1919, 243A.

[9] Eng. Pat. 127933 ; *J.*, 1919, 565A.

from the upper section and power gas from the lower, may be kept separate.

Low Temperature Carbonisation.

The process of low temperature carbonisation continues to receive considerable attention now that the question of fuel economy is under review. This process has much to recommend it, for in spite of the recently discovered mineral oil deposits in this country, it is evident that every economic source of obtaining fuel oils and allied products is of national interest. Moreover the large scale production of a household fuel more desirable than gas coke to displace completely the use of raw coal is of vital interest. The great disadvantage of most low temperature coke is its friable nature and the consequent marked deterioration which occurs during its transportation. In dealing generally with the subject of fuel economy H. E. Armstrong [10] in an address to the British Scientific Products Exhibition states that in drawing up a comprehensive scheme for coal conservation, the utilisation of every product that can economically be extracted from the coal, together with the provision of a smokeless fuel for public use, constitute the two most important objects to be kept in view. He foreshadows a future system in which oil, power, fuel, and ammonia are produced, together with a rich gas suitably diluted with water gas as a secondary product. A system of carbonisation coupled with the generation of electricity involving the fusion of the gas and electric interests has been suggested by Armstrong and many other prominent scientific men as the road to true fuel economy.

Low temperature distillation is carried out in an experimental plant at Denver, U.S.A.,[11] in which coal, ground to pass a 20-mesh screen, is compressed during distillation through a vertical retort 18 feet long and 18 inches diameter. A spiral fin cast on the outer surface of the retort breaks up the currents in the ascending heating gases, and assists in absorbing the heat therefrom, and in conveying it to the contents of the retort. The coal which is fed continuously into the top of the retort is first agitated and then forced downwards by means of a hollow worm centrally mounted within the retort, whilst the gases evolved during the carbonisation escape through openings into the interior of the worm. Each retort contains at any period 250 lb. of coal and 25 tons are carbonised per 24-hour day. One-half of the gas yield of 4000–6000 cub. ft. of 700 B.Th.U. per ton is used in the process for heating purposes. In attempting to overcome the difficulty of the friability of the coke resulting from these processes, Summers [12] carbonises large masses of non-coking coal in a coke oven fitted with a reciprocating floor for discharging. It is claimed that owing to the large

[10] J., 1919, 265R.   [11] Gas World, 1919, 71, 57.
[12] Times, Eng. Suppl., Aug., 1919, p. 250.

mass undergoing carbonisation and the high pressure existing in the lower layers of the retort, the coke produced is relatively dense. A similar plant is being prepared for demonstration purposes in this country and detailed results may be expected during the coming year. The "Carbocoal" process developed at Irvington, New Jersey, by C. H. Smith [13] has been worked out in considerable detail. The process, although somewhat involved, incorporating as it does three distinct phases, namely, (1) low temperature carbonisation, (2) briquetting of the low temperature coke, and (3) high temperature carbonisation of the briquettes, appears to have attained a fair measure of success. The pulverised coal is carbonised with constant agitation at about 450° C., and " Semi-carbocoal " is produced. This product is briquetted with the pitch derived from the distillation of tar produced from both the primary and secondary carbonisation, and is then subjected to the secondary carbonisation at 1100° C. The final product "Carbocoal" is dense, clean, uniform in size and quality; it burns readily and is stated to be a suitable smokeless fuel. The yield of Carbocoal is about 72% by weight of the coal treated, the yield of gas being 5000–6000 cub. ft. of 650–700 B.Th.U. gas from the first operation and 4000 cub. ft. Of 350–400 B.Th.U. gas from the second operation. The analysis of Carbocoal obtained from washed coal is : moisture, 1–3% ; volatile matter, 0·75–3·5% ; fixed carbon, 85–90% ; ash, 7–10%, and sulphur 0·6–1·5%. The tar resulting from the first distillation amounts to about 14–16 imperial gallons per ton of coal, while 4–6 gallons are produced from the second distillation : ammonia, to the extent of 20–24 lb. sulphate of ammonia is recovered.

The difference in composition of the tar obtained from the primary and secondary carbonisation is shown in the following table :—

	Primary carbonisation.	Secondary carbonisation.
	galls.	galls.
Light oils, up to 170° F.	1·06	0·002
Middle oil, 170°–230° F.	2·20	0·024
Creosote, 230°–270° F.	2·08	0·084
Heavy oil, 270°–360° F.	5·92	1·656
Pitch	4·60	2·194
Loss .	0·14	0·040
	16·00	4·000

The whole of the pitch and gas are used in the process, and the

marketable products are thus Carbocoal, motor spirit, fuel and lubricating oils, and ammonium sulphate.

There should be an interesting future for a process based upon such a combined low and high temperature distillation.

THE REMOVAL OF TAR AND THE EXTRACTION OF AROMATIC HYDRO-CARBONS FROM THE GAS.

Electrical Separation of Tar.

The electrical precipitation of tar fog from hot gases by the Cottrell method is becoming more extensively used where electricity is obtained at a cheap rate. J. G. Davidson [14] states that where direct ammonia recovery is practised, the method effects an appreciable saving in fuel, as it is unnecessary to cool the gas and thus a large proportion of the apparatus generally installed for direct ammonia recovery is avoided. In an experimental plant of 1 million cubic feet per day working capacity, the author finds the total power consumption to be 2 3 h.p. and that the process effectively deals with the hot vapours from the distillation of wood, coal, and petroleum.

Extraction of Benzol, etc.

Since the signing of the armistice and the conclusion of hostilities, the extraction of benzol and toluol from coal gas has been less generally practised. In view of the proposition to sell gas on a thermal basis the whole question has now resolved itself into one of economics. The factors which require consideration by the gas manufacturer are (1) the market value of benzene as a motor spirit, (2) the extent to which benzene removal affects the proportion of water gas that can be added to produce the stipulated calorific power of the gas to be supplied, and (3) the selling price of gas on the thermal basis. It is generally considered to be financially unsound to extract these hydrocarbons under the present market conditions.

E. Sainte-Claire-Deville [15] has contributed a most valuable paper on benzol in coal gas, in which is reviewed experimental work carried out for over 30 years at the Experimental Works of the Paris Gas Company. In this paper all the hydrocarbons in the aromatic series, from benzene to cymene, are termed " benzol," while the term " benzine " denotes the mixture of light hydrocarbons distilling from 79° to 83°–84° C.

The work on the estimation of benzol is based on preliminary experiments in which is determined the weight of benzine taken up by a given volume of gas at 0° and 760 mm. Gas containing benzine is passed through a series of weighed coils maintained at different temperatures, that of the first coil being 0° C., of the second and third

[14] Trans. Canadian Min. Inst., 1918, 21, 252 ; J. 1919, 315A.

[15] Gas J., 1919, 147, 392.

—21·7° C., and of the final condenser —70° C., and in this way the whole
of the benzine is removed from the gas. From a series of experiments
it was determined that after cooling to —21·7° C. the benzine content
of the gas is constant at 10·3 grains per cub.,ft. On the assumption that
the hydrocarbons condensing at —70° C. exist in average gas to the
amount of 10·3 grains per cub. ft., and those condensing at —21·7° to
the amount of 7·1 grains (an average figure for a number of tests),
1 cubic foot of normal gas contains 17·3 grs. of benzol of composition
indicated in the following table :—

	B. pt , °C.	Composition, % by weight.
Distillate lighter than benzine . .	70° - 80°	2·2
Benzine, pure	79°- 84°	75·9
Benzine, toluene, etc., not separable	84°–105°	9·41
Benzol Toluene	105°–115°	5·81
Xylene, cumene, etc. .	115° 165°	5·76
Viscous residue, heavy oil, etc.	—	0·92

In practice, the method of condensing at —21·7° C. as a means of
estimating the benzol of gas ceases to be accurate as soon as the benzol
content falls below 11·8 grains per cub. ft., as for instance in debenzolised
gas and gas produced at the end of carbonisation.

The removal of benzol at —70° C. lowers the illuminating value by
65% and the calorific power by 7·20%.

As regards the solubility of benzol in water the author finds that
equilibrium is established between the vapour tension of the benzol
in the gas and in the water when the water contains 61·4 grains of
benzol per gallon, and concludes that a holder, the water of which remains
saturated for a long time, affects the mean benzol content of the gas to
only a negligible extent.

The tar present in the condensers, etc., acts as a reservoir of benzol,
as is shown by the following table :—

	Gas before entering condensers and purifier. Benzol per cub ft. Grains	Gas after passing through condensers and purifiers. Benzol per cub. ft. Grains.
First hour of carbonisation . . .	21·4	17·3
Second ,, . ,, . . .	19·3	15·4
Third ,, ,, ,, . . .	12 3	18·8
Fourth ,, ,, . . .	4·6	19·1

From these figures it is evident that the tar absorbs benzol in excess from the gas at the beginning of the charge, and gives it up at the end of the charge.

F. Soddy [16] finds that at ordinary temperatures 1 ton of charcoal serves to remove the ethylene from 10,000 cub. ft. of coal gas, the ethylene absorbed amounting to about 1% by weight of the charcoal. The avidity of charcoal for benzene is so great that it will absorb benzene from gas already treated by the oil-washing process, to the extent of 10—15% of its own weight.

In the process patented by this author for the removal of the illuminants and impurities in coal gas by means of charcoal, continuous or intermittent working may be adopted. The continuous process is based on the principle that the more volatile compounds which are at first absorbed may be replaced by the less volatile compounds as the passage of the gas is continued. In order to effect the removal of illuminants, sulphur compounds such as carbon bisulphide and hydrogen sulphide as well as carbon dioxide and water vapour should previously be removed from the gas, and when the extraction of ethylene is the main object to be attained there should be a preliminary treatment for the removal of benzene. The absorbing power of charcoal gradually decreases owing to the absorption of carbon dioxide and other dense gases, and the retarding effect becomes pronounced when the process is installed for the removal of ethylene.

The absorbed illuminants are expelled from the charcoal at elevated temperatures, the temperature of evolution of ethylene being somewhat lower than that of benzene.

Owing to the low thermal conductivity of charcoal and the difficulty of heating large masses, it is desirable to operate with thin layers, and especially is this necessary in the intermittent process. Given a reliable working process for the oxidation of ethylene to alcohol, the process must assume considerable importance.

AMMONIA AND CYANOGEN.

Ammonia.

Interest continues to be centred on processes which simultaneously extract ammonia and hydrogen sulphide from the gas for the direct production of sulphate of ammonia. In the process devised by J. W. Cobb [17] the crude gas is conducted through a solution of zinc sulphate, the resulting zinc sulphide being filtered, and the mother liquor concentrated for the recovery of ammonium sulphate. The zinc sulphide thus obtained is roasted and the acid products of combustion, together with an excess of air, are blown through water containing in suspen-

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[16] Eng. Pat. 125253; *Gas J.*, 1919, **146**, 379; *J.*, 1919, 352A.

[17] *Gas World*, 1919, **71**, 80.

sion the zinc oxide from a previous roasting, whereby zinc sulphate is regenerated and the cycle of operations completed. With regard to the direct system of ammonia recovery, W. S. Curphey [18] states that the ammonia losses are still excessive, and may be attributed mainly to two causes, the lack of skilled attention to the primary still, and the necessity for passing some ammonia to the oxide purifiers to facilitate the complete removal of hydrogen sulphide from the waste gases. Curphey has recently patented a modification of the direct ammonia recovery process which should present many advantages.

K. Liese [19] has stated that although much work has been done in past years on the subject of simultaneous recovery of hydrogen sulphide and ammonia, the processes introduced are so cumbersome and unreliable in practice that they are not superior to the older methods of absorption of ammonia in water, and removal of hydrogen sulphide by oxide of iron. In the paper in question Liese makes certain recommendations anent existing gas-works plant with regard to the prevention of blockage in the upper tiers of filling material in scrubbers, and to the advisability of employing water sprays as an adjunct to the gas scrubber. It should here be remarked that chemists of the gas industry are not generally in accord with this author's statement, for the crude arrangements at present in vogue for extraction of ammonia and hydrogen sulphide leave much room for improvement.

F. Sommer [20] has investigated the temperature conditions for the maximum yield of ammonia, and in accordance with many other investigators, finds a range of 800°–900° C. to be most suitable. The distribution of nitrogen at this temperature is as follows :—

	Westphalian coals	Silesian coals.
Most favourable temperature of distillation	800°–850° C.	900° C.
Nitrogen in dry ash from coal . .	1·896%	1·5485%
„ in ammonia	17·85%	19·19%
„ in hydrocyanic acid . .	0·47%	1·05%
„ in tar	1·63%	2·66%
„ in coke	73·23%	60·32%
„ in gas (by diff.) . . .	6·82%	16·78%

The yields of ammonia in practice are dependent upon various factors, such as the rate of increase of temperature, the maximum tempera-

[18] Gas World, 1919, 71, 81.

[19] J. Gasbeleucht., 1919, 62, 113 ; J., 1919, 277A.

[20] Stahl u. Eisen, 1919, 39, 261, 294, 349 ; J., 1919, 350A.

ture of the products of distillation, and the time during which they are in contact with the hot oven walls. The following table illustrates how these factors vary according to the type of oven employed :

Type of carbonising chamber.	Weight of charge in tons	Carbon-ising period in hrs	Temp C	Slowing wall area per ton of coal in sq ft	Time of action in seconds.
Horizontal retorts .	0·118	5	1165	290	112·3
Vertical ,, .	0·50	7	1150	176	2·4
Horizontal chamber .	10·3	24	1100	68·3	3·4
Sloping chamber . .	6·6	24	1050	83	2·3
Coke ovens . . .	7·28	30	1000	84	8·4

For the purpose of efficient recovery of ammonia Sommer considers horizontal retorts to be unfavourable in every respect, as the relatively high temperature obtained and the subsequent slow rate of cooling (as indicated in the above table) are conditions quite unsuitable for the production of ammonia. He further advocates the use of steam for conserving the yield of ammonia, especially during the latter half of the distillation period. Oxygen has a powerful destructive action on ammonia ; it is demonstrated that oxidation of ammonia by air begins at 150 C. and that a mixture of 2·2% of ammonia in dry air is oxidised to the extent of 5·86% at 250° C., whilst in the presence of 2·3% of steam only 0·89% of the ammonia is oxidised. Similarly while 12·89% of the ammonia is oxidised at 450° C. in the case of dry ammonia air mixture, only 2·01% is decomposed if the air be moist. The presence of hydrogen sulphide is also considered to be a deterrent to oxidation, it being more readily oxidised than ammonia. Here again, steam may play an important rôle, for by its reaction with sulphur in the coke the concentration of hydrogen sulphide is maintained. Briefly summarised the three essentials for producing high ammonia yields are (1) rapid removal of gases from the zone of high temperature, (2) presence of steam, (3) absence of oxygen.

H. Salmang [21] in an interesting paper on the production of ammonia by the complete gasification of coke in the presence of air and steam, states that from 73 to 95% of the nitrogen is recovered as ammonia in the presence of steam and air at 900" C., this proportion being increased to 81–96% in the presence of lime. An important conclusion arrived at by the author is that during this process the ratio carbon : nitrogen remains constant. The corollary to be drawn from this is that the

[21] Z. angew. Chem., 1919, 32, 148 ; J., 1919, 4.5.A.

nitrogen of coke cannot be converted to ammonia unless the coke is completely decomposed.

Cyanogen.

The main interest centring around the recovery of this constituent of the gas lies not so much in the value of the product 'or the manufacture of cyanides, but because its presence in the gas has a deterrent action on oxide purification, as well as a destructive effect upon metals. Cyanogen recovery should therefore be considered a necessary adjunct to the gas purification processes. The latest polysulphide plants are capable of removing 95–98% of the total hydrocyanic acid in coal gas.[22] E. Ciselet and C. Deguide [23] have patented a process for the simultaneous removal of cyanogen, hydrogen sulphide, and carbon dioxide from coal gas by the use of restricted quantities of ammonia and lime. The ammonia reacts with the acid gases, ammonium carbonate, sulphide, and cyanide being formed, which by double decomposition with the lime present are converted into calcium salts with the liberation of ammonia. The ammonia is therefore being constantly regenerated, and may serve continuously for purification as long as the quantity of lime is not exhausted   W. Feld [24] has introduced the following modifications in the methods of cyanogen recovery usually practised :- -

1. The use of a ferrous salt and calcium hydrate to give the reaction :

$$FeSO_4 + 3Ca(OH)_2 + 6HCN = CaSO_4 + Ca_2Fe(CN)_6 + 6H_2O.$$
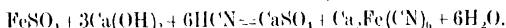
2. The use of salts of which the corresponding oxides are displaceable by ammonia. A typical reaction of this process is :—

$$2MgCl_2 + 4NH_3 + 6HCN + Fe(OH)_2 = Mg_2Fe(CN)_6 + 4NH_4Cl + 2H_2O.$$
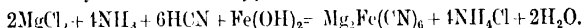
3. By the use of iron already combined with cyanogen :

$$3Fe(CN)_2 + 6Ca(OH)_2 + 12HCN = 3Ca_2Fe(CN)_6 + 12H_2O.$$

Feld prepares pure cyanides from coal gas by first washing with hot solution of magnesium hydroxide to remove carbon dioxide, then with a solution of lead, manganese, or iron to remove hydrogen sulphide, and finally with a cold solution of magnesium hydroxide to remove hydrocyanic acid. By simply boiling the product of the last reaction pure hydrocyanic acid is obtained.

REMOVAL OF HYDROGEN SULPHIDE AND SULPHUR COMPOUNDS.

Hydrogen Sulphide.

Certain contributions have been made towards a more complete knowledge of the oxides and hydrates of iron, and their behaviour towards hydrogen sulphide. G. Weyman [25] states that under the conditions of gas-works practice the sesquisulphide is usually produced.

[22] Chem. Age, 1919, **1**, 91-92.
[23] Engg Pat. 9780, 1915; Gas J., 1919, **146**, 761.
[24] Gas World, **70**, 517.   [25] J., 1918, 333T.

There would appear to be only a small proportion of monosulphide produced in this process, and this at higher temperatures of working may combine with sulphur, resulting in the formation of disulphide. After oxidation of the purifying mass the quantity of ferrous sulphate present has certainly increased although there is no direct evidence to show that this originates from the oxidation of disulphide. The reduction of purifying efficiency of oxide even when maintained in an alkaline condition is considered to be due partly to the production of ferro-cyanides and of disulphides, and to the dilution of active oxide by reason of the sulphur absorbed. The author further shows that oxide of iron does not become inactive towards hydrogen sulphide until heated to a temperature of $800°$ C. The results obtained apparently refer to the use of hydrogen sulphide in high concentration, and it would be of interest to ascertain whether the same conditions are maintained with hydrogen sulphide at a concentration of 1-2%, which would bring the research into line with industrial practice. The result of experimental work has led the author to the conclusion that the activity of oxide of iron is primarily dependent upon molecular structure, and not upon the particular degree of hydration, although the final molecular structure may be determined by the hydrated condition in which the material at one time existed. The method of cooling the oxide probably plays an important part in the question of its final activity as regards the absorption of hydrogen sulphide, for it was found that the activity of o de which had been heated for three hours at $800°$ C. and plunged into cold water had increased from 1% to 43%, as compared with a slowly cooled sample of the same oxide. The author formulates an hypothesis by which it is assumed that the molecules of oxide which at $800°$ C. are in a mobile state rearrange themselves on slow cooling in a more condensed form. This assumption is borne out by the determinations of the specific gravity of the material after heating to varying temperatures, the specific gravity being found to rise steadily with each increase in temperature. It is upon this ground therefore that sudden cooling of the heated material is recommended.

The Chief Alkali Inspector in his annual report [26] states that the "backward rotation" system with downward flow has fully justified itself as a means of operating a purifying system. This is particularly the case if the efficiency of the process is measured by the absolute volume of hydrogen sulphide absorbed by the oxide prior to its final discharge and by the capacity of the material to deal with variations in the make of gas. As by the adoption of this system the purifying material is operated under more favourable conditions, the necessity for by-passing small amounts of ammonia from the scrubbing system is obviated and consequently an increased yield of ammonia is obtained. Various suggestions for the more scientific control of oxide purification

[26] See *Gas World*, 1919, **71**, 80.

have been made as a result of investigations carried out on the direct process of sulphate of ammonia manufacture. These suggestions refer to the regulation of temperature, the ammonia content of the crude gas, and the humidity of the oxide. Curphey finds it difficult to correlate rises in temperature of the working oxide mass with the work done as measured by the make of sulphur, owing to such varying influences as radiation losses, local evaporation and condensation of water vapour within the boxes and connecting mains, etc. At the same time he is of opinion that variations of temperature in a given layer afford a valuable indication as to the activity of the material, and are particularly useful in anticipating periods of disorganisation.

It has been suggested that the small proportion of oxygen that must of necessity remain in the gas when regeneration *in situ* is practised exerts a destructive effect upon the cast-iron mains and services, more particularly in those cases where the complete extraction of naphthalene from the gas constitutes an integral factor of the purification system. In view of this suggestion it will be of interest to note that attempts have been made both in this country and in America to revivify the oxide by injecting air through the material after the box has been isolated from the gas stream. Owing to the liability of the mass to become overheated during its regeneration this process requires careful operation. F. W. Steere [27] arranges a blower connected in closed circuit with the purifier and by this means circulates air at three times the normal velocity of the gas. This is quickly diluted, and the loss of oxygen can be replaced by fresh air, which is admitted in such quantities as will maintain a safe temperature within the mass undergoing revivification.

H. G. Colman and E. W. Yeoman [28] have contributed valuable work on the subject of the valuation and methods of analysis of spent oxide.

An American writer [29] describes a method successfully used for removal of hydrogen sulphide from gas containing a considerably larger proportion than coal gas. The process depends upon the circulation of water containing precipitated hydrate of iron in suspension through two towers of similar construction to the normal gas-works scrubber, the lower end of each tower being open and sealed in a large tank containing the purifying suspension. The iron in the mixture in the tanks is prevented from settling by air agitation, the oxygen required for revivification being also obtained from this source.

Sulphur Compounds other than Hydrogen Sulphide.

E. K. Rideal and H. S. Taylor [30] have recently patented a modifica-

[27] *Gas J.,* 1919, **146,** 303.
[28] *Gas J,* 1919, **145,** 68, 112, 169; *J.,* 1919, 103A.
[29] *Gas J.,* 1919, **146,** 495.
[30] Eng. Pat. |30654; *Gas World,* **71, 203**; *J.,* 1919, 710A.

tion of the catalytic process for the removal of carbon bisulphide in which the catalytic material employed is comprised of oxide of iron admixed with suitable proportions of one or more of the oxides of chromium, nickel, cobalt, cerium, thorium, zirconium, manganese, or molybdenum. By the use of this catalyst, together with a suitable proportion of water vapour, the oxides are not reduced by the heated coal gas, neither is the hydrogen sulphide produced in the reaction absorbed by the catalyst. The reaction temperature varies between 300° and 650° C., according to the composition and sulphur content of the gas and nature of the catalyst employed. An efficiency of 90% is claimed.

Charcoal, in addition to serving for the removal of illuminating hydrocarbons, is also being adopted for the extraction of carbon bisulphide and naphthalene. A process based on the absorption of carbon bisulphide by charcoal should possess special advantages over the catalytic processes inasmuch as the subsequent use of oxide purifiers is of course unnecessary. W. G. Adam [31] has patented a process for the simultaneous removal of carbon bisulphide and naphthalene from coal gas, and for this purpose conducts the gas from the usual purification system through granular charcoal contained in vessels similar to oxide purifiers. The quantity of charcoal required depends upon its activity and the amount of impurities in the gas. It is stated that 70 lb. of charcoal per 12,000 cub. ft. of gas (equivalent to one ton of coal carbonised) reduces the sulphur content of gas from 35 to 7 grains per 100 cub. ft., and entirely removes the naphthalene originally present in the gas to the extent of 6 grains per 100 cub. ft. Both the carbon bisulphide and naphthalene are recovered by heating the spent charcoal to 300° C.

NAPHTHALENE.

Although many of the difficulties relating to naphthalene stoppages in the mains and services of gas undertakings have disappeared with the cessation of the process of naphtha recovery from coal gas, the disability under which the industry labours in respect of the trouble and annoyance caused by the deposition of this hydrocarbon has not disappeared. There seems to have been no distinct modification of the process adopted for the complete removal of naphthalene from coal gas. or of those processes involving the injection of an oil spray to prevent the deposition of naphthalene. As to the relative merits of these two methods of dealing with the problem, the general opinion is held that although the complete extraction of naphthalene from the gas before it leaves the works is to be recommended, it carries with it the disadvantages that many years are required before the mains and services are completely

[31] Eng. Pat. 127431; *Gas World*, 71, 44; *J.*, 1919, 566A.

cleared from naphthalene by the purified gas, and it is therefore suggested that this process should be accompanied by one of oil spraying in order to reduce this period.

TAR DISTILLATION AND DEHYDRATION.

F. W. McNear,[32] C. W. McKibben,[33] and others have introduced processes for the electrical dehydration of tar. In one form of plant the emulsion flows through a successive series of annular electrodes and round a series of discs between which an electric field is maintained, whilst in another plant the emulsion is subjected to a continuous and uniform electrical field. In the latter case the velocity of the emulsion is sufficient to cause the polarised water globules to cohere and thus separation is effected.

R. Weissgerber and O. Kruber[34] conclude from an investigation of the heavy oil fraction of coal tar boiling between 260°–265° C., that contrary to the general opinion it is not deficient in solid matter. The authors have isolated three solid dimethylnaphthalenes, from this fraction—2.3-, 2.6-, 2.7-dimethylnaphthalene—the β-methyl and 1.6-dimethylnaphthalenes being the only genuine oils present.

F. Ruszig[35] finds that so-called anthracene oil yields brown dye-stuffs analogous to the methyl- and phenyl-xanthenes and suggests that anthracene oil contains certain triphenylmethane derivatives, and in particular phenyl- and diphenyl-xanthenes. The hydrochlorides of the brown dyestuffs are soluble in water and act as direct dyes for wool and silk.

J. M. Clark[36] describes a method of separating the solid obtained by cooling anthracene oil, which consists mainly of a mixture of anthracene, carbazole, and phenanthrene. The solid is mixed with crude coal tar naphtha heated to 80° C., and by cooling to 30° C., and filtering at this temperature, the major portion of phenanthrene is recovered in the filtrate. Pure phenanthrene is prepared from this extract by a second naphtha treatment, followed by fusion with alkali hydroxides, distillation, and then by further treatment with naphtha and decoloration with bone black. The pure product is finally obtained by crystallisation from alcohol.

The solid residue from the previous filtration is mixed with light pyridine, heated to 80° C., cooled, and filtered at 15° C. At this stage the soluble portion consists largely of carbazole and the insoluble residue is chiefly anthracene. The soluble portion is separated and subjected to a second naphtha washing, and by sulphonatic.1 and solution in

[32] U.S. Pat. 1297378 ; *J.*, 1919, 403A.
[33] U.S. Pats. 1299589 and 1299590 ; *J.*, 1919, 403A.
[34] *Ber.*, 1919, **52**, 346 ; *J.*, 1919, 455A.
[35] *Z. angew. Chem.*, 1919, **32**, 37 ; *J.*, 1919, 217A.
[36] *J. Ind. Eng. Chem.*, 1919, **11**, 204 ; *J.*, 1919, 247A.

water the anthracene is removed, and 99·5% carbazole prepared from the insoluble residue by sublimation. 99·9% anthracene is prepared from the insoluble anthracene residue by repeating the pyridine treatment, and by sublimation, distillation after fusion with alkali hydroxides, and crystallisation from benzol.

Detailed information as to the nature of tar produced during low temperature distillation of coal is scarce. F. Fischer and W. Gluud [37] by using a revolving furnace avoid the superheating of products of distillation and obtain considerable quantities of tars which are characterised by the presence of naphthenes, highly viscous oils, and paraffin wax, and by the absence of aromatic compounds. Gas coal and cannel coal yield 10% and 14% of tar by weight respectively, whilst gas coals in tar recovery producer systems yield 15% of tar. The following table is given as a contribution to the knowledge of the composition of these tars :- -

| | Tar from low temperature distillation | | Tar from producer systems |
	Bituminous coal.	Gas coal	Gas coal
	%	%	%
Non-viscous oils . . .	33·5	15·0	17·7
Viscous oils (lubricants) .	15·2	10·0	11·3
Phenols	11·0	50·0	37·8
Solid paraffin	0·1	1·0	0·8
Resins	1·2	1·0	0·7
Pitch	19·2	6·0	15·0
Loss and water . . .	13·5	17·0	16·7

It would appear that the tars derived from complete gasification systems possess many of the characteristics attributed to low temperature tar.

COKE AND COKE OVENS.

Whilst there must always be a certain demand for metallurgical coke in this country, the future of coke manufactured as a by-product of the gas-making process is a question which should receive most careful consideration. Gas coke, although eminently suited for the production of steam power, cannot be considered to be entirely successful as a household fuel. For household purposes it is to be anticipated that the gas-works coke will find strong competition from that produced by low temperature distillation, and the serious rise in the ash content

[37] *Ges. Abhandl. Kennt. Kohle*, 1917, 1, 114; *J.*, 1919, 492A.

of coke resulting from the extensive steaming of the retort charge is therefore regarded with alarm in some quarters. The consequent extra clinkering, removal of clinkers, and the high proportion of unburnt fuel in the clinkers caused by the use of fuels containing a high percentage of ash, must assuredly act unfavourably upon the sale of the product. On the other hand, it is stated that very moderate steaming of the charge produces a coke of high porosity which is more adaptable for general fuel purposes, it being also more easily ignited. Further, the ash content is increased to such a slight extent as to present no difficulties.

With regard to metallurgical coke, Myers.[38] in dealing with the preparation of coal for coking, emphasises the importance of adequate selection and treatment of coal used for this purpose. In this paper coals are classified under three main headings, (1) large lumps, (2) good quality slack, and (3) slack which requires washing. The major portion of the paper deals with this latter class, as such coals constitute the largest proportion of coking fuels used in this country at the present time. From a consideration of the theoretical principles of coal washing, the author determines that particles of shale of sp. gr. 2·3 and 0·3 in. in diameter obtain the same limiting velocity in water as a particle of coal sp. gr. 1·3 and 1·3 in in diameter. The maximum ratio of diameters is 4·3 : 1, and thus it would appear to be impossible to separate particles of coal and dross of respective diameters 4·3 and 1 without a preliminary sizing. Various types of modern washing plant are discussed. The use of clear water of the correct sp. gr. is considered to be a most important factor, as it affects not only the separation of dross, but also the removal of soluble salts and alkalis from the coal. W. J. Rees [39] has examined the nature of these soluble salts and their corroding effect on coke oven walls, and finds as the result of analyses of the pumpings from shallow workings, the circulating water at the washeries, and the drainings from the washed slack hoppers, that a comparatively large proportion of inorganic salts can be removed by adequate washing. The sodium salt content of washed and unwashed slack is shown to be as follows :—

	Washed	Unwashed
Sodium chloride	0·18%	0·37%
Sodium sulphate	0·08%	0·19%

It is stated that although the extra expenditure involved in substituting pit water by town water to reduce further the soluble salts would not appear to be justified, it is frequently advantageous to increase the volume of water circulated at the washery in order to reduce the salt content of the water adhering to the slack. The rate of flow of water

[38] *Gas World (Coking Section)*, **71**, Aug. 2, p. 12.

[39] *Gas World (Coking Section)*, **70**, June 7, p. 18.

through the washery is probably a factor of greater importance in reducing the salt content of this adhering water.

There is a general tendency to employ for heating purposes producer gas made from coal slack in ammonia recovery plants in place of coke-oven gas, and to divert the high calorific power gas manufactured for town supply or for such commercial purposes as furnace heating, etc. Perhaps the greatest difficulty to be encountered in the distribution of coke-oven gas for town purposes will be that of ensuring a constant supply. It is not the practice of a coke-oven works to store large quantities of coal owing to deterioration affecting the quality of the coke—the coke of course being the product requiring main consideration—and hence it is difficult to ensure a continuous and regular supply of gas in view of a possible shortage of coal and the difficulties of transport.

INCANDESCENCE MANTLES

H. E. Ives, E. F. Kingsbury, and E. Karrer [10] have investigated the spectral distribution of the luminous radiation from incandescence mantles containing various mixtures of thoria with other oxides. The characteristic features of the luminous radiations in the case of the thoria-ceria mixtures are exhibited by various other mixtures but in different degrees. The thoria-ceria mixture which yields the maximum luminous radiation contains 0·75% of ceria, and is obtained with a flame adjusted with its outer edge just inside the mantle. Luminous radiation is decreased and heat radiation increased by forcing the flame through the mantle. In the case of a black body colorant the authors calculate that whilst the total radiation varies as the 4th power of the temperature, the luminous radiation varies as the 11th or 12th power in the region of 1800° C. From this it is deduced that it is more economical from the standpoint of light radiation to heat a small quantity of matter to a high temperature than a large quantity to a low temperature. This is proved in practice, but as the durability of the mantle depends largely upon its weight, a compromise has to be made between durability and efficiency. The ideal to be sought from the standpoint of light production is that the heated body shall yield a maximum emissive power in the visible region of the spectrum, concentrated on the wave lengths of maximum visibility. The maximum possible efficiency attainable by heating a mantle in the customary manner is 2·6%; the efficiency at present realised with incandescence mantles is 0·19%. For all mixtures efficiency is increased with increased temperature, and thus for ceria mixtures the limit is set at about 1950° C., the melting point of ceria.

J. S. G. Thomas [41] shows that the increased efficiency of the inverted

[40] *J. Franklin Inst.*, 1918, **186**, 401, 585; *J.*, 1919 167A.
[41] *J.*, 1919. 168T.

over the upright system of gas lighting is to be attributed to the higher
temperatures obtained due to heat regeneration effected by the rising
products of combustion. By circulating water in the regions of the
nozzle and injector, and thus maintaining the combustible gaseous
mixture at a relatively low temperature, the mean radial candle power
of a No. 3 Metro burner is reduced from 75·6 to 51·7 candles.   On the
other hand by preheating the combustible mixture fed to an upright
burner the lighting efficiency is increased in a horizontal direction
from 66·1 to 100·2 candles. The following results may be quoted :- -

No. 3 Metro Burner.

	Without water cooling	Region of Injector water-cooled	Nozzle and region of injector water-cooled
Gas consumption (cub. ft. per hr.)	3·85	3·81	3·85
Primary air (cub. ft. per hr.) . .	10·29	10·21	10·26
Ratio primary air : coal gas . .	2·67 : 1	2·66 : 1	2·65 : 1
Horizontal candle power . . .	57·1	58·4	40·6
Candle power at 50° below horizontal	81·9	81·2	58·0
Mean radial candle power . .	75·6	73·3	54·7
Candles per cubic foot at 50° below horizontal	21·3	21·1	15·1
Mean radial candles per cub. ft. of gas	19·6	19·1	14·2

Upright Incandescence Burner.

Temp. of gas and primary air mixture prior to combustion	Gas consumption (corrected to 30 in and 60° F).	Primary air (corrected to 30 in and 60° F).	Ratio, primary air to gas.	Candle power in horizontal direction	Horizontal candle power per cub ft of gas.
°C.	Cub. ft.	Cub. ft.			
70	4·80	11·7	2·44	66·1	13·8
110	4·80	11·7	2·44	68·0	14·2
130	4·80	11·8	2·46	69·1	14·4
150	4·80	11·9	2·48	72·8	15·2
190	4 80	12·0	2·50	78·6	16·4
216	4·80	12·0	2·50	87·8	18·3
220	4·80	11·9	2·48	92·5	19·3
225	4·80	12·0	2·50	98·3	20·5
245	4·80	11·8	2·46	99·5	20·7
270	4 80	12·0	2·50	100·2	20·9

The highest temperature to which the mixture can be preheated is found to be 270° C. The primary air supply alone was preheated and mixed with the combustible gas. Attempts made to obtain a higher temperature of preheating of the mixture resulted in slight decomposition of certain hydrocarbon constituents of the gas. Further work should be carried out in the direction of ascertaining the effect of preheating to higher temperatures gases which are not subject to this decomposition.

CHEMICAL AND PHYSICAL CHARACTERISTICS OF COAL GAS.

The studies carried out and the recommendations made upon this subject during the past year are of the greatest importance, and may be said to have contributed in a greater measure than any other work to the creation of that sound basis upon which the gas industry is to develop. Cobb and his co-workers, experimenting along the lines suggested by the Gas Investigation Committee of the Institution of Gas Engineers, have continued work upon the relative efficiencies of gases of varying calorific power when used in the lighting and heating apparatus to be found upon the market. The second report of the Research Sub-Committee [42] records the results of a series of efficiency tests carried out with ring burners and with upright and inverted incandescence burners on gases varying in calorific value from 385 to 391 B.Th.U. per cub. ft. The results obtained with ring burners which were suitably adjusted show that a gas of this low calorific value gives as good a thermal efficiency as any other grade of gas previously tested, and that the value of different gases in ring burners is directly proportional to their calorific powers. In all cases the only modification required to render existing appliances suitable for use with this gas was the enlargement of the nipple orifices The latter part of the Report is a direct continuation of the lighting section of the first Report [43] and deals with the relative efficiencies in use of the different grades of gas. Experiments were made with mixtures of coal gas and blue water gas in various proportions, yielding gases of from 291 to 618 B.Th.U. per cub. ft. These experiments were carried out with a normal upright burner, no alterations being effected in the burner for the different grades of gas. The anticipated efficiency of from 27 to 28 P. . h U. per candle hour was obtained and in some cases exceeded, but the experiments show that completely satisfactory comparisons of these different gases can only be made when each is permitted to exercise its maximum duty in an appliance properly adapted to its use.

This experimental work is being continued and at the present moment a study is being made of the effect of the inert constituents of coal gas upon the illuminating power developed by the incandescence mantle.

[42] *Gas J.*, 1919, 146, 607; *J.*, 1919, 524A.   [43] *J.*, 1918, 681A.

Not only does there appear to be no evidence which would refute the original finding of this Sub-Committee, namely, that the value of gas to the consumer is, for general purposes, in direct proportion to its calorific power, but the results obtained generally confirm this conclusion.

Shortly following the enunciation of this principle C. Carpenter [44] suggested that it would be directly in the interest of the consumer that gas should be sold on the basis of its thermal value rather than by volume, and pointed out that the acceptance of such a principle must eventually be beneficial to the gas industry.   He suggests that as regards the new standards to be adopted 10,000 B.Th.U. should represent a therm, and that the standard gas unit should be a decatherm or 100,000 B.Th.U. He further deals at length with the modifications to the existing systems of gas sales which would have to be adopted under the proposed scheme.

Soon after the formulation of the above proposition the Fuel Research Board issued its report on the question of gas standards to the Board of Trade. In this report the Board recommends the sale of gas on the basis of heat energy on the same plan as outlined by Carpenter. Other important recommendations refer to the necessity of adjusting consumers' appliances in order to obtain the maximum efficiency, to the inadvisability of diluting coal gas with inert gases, and to the more complete removal of hydrocyanic acid and sulphur compounds other than hydrogen sulphide. Later in the year as the result of a conference between consumers, gas undertakings, and local authorities, the recommendations made in the report of the Fuel Research Board were accepted with certain amendments. These recommendations and embodied amendments are as follows :—

(1) That the proposed system of charging the consumer for the potential thermal units supplied to him is accepted.

(2) That the thermal units chargeable are to be calculated by multiplying the number of cubic feet registered by the consumer's meter by the declared gross calorific value of the gas per cubic foot.

(3) That the calorific value of the gas is to be continuously measured and recorded by a recording calorimeter of a standard type, to be passed by the London Gas Referees. That the method of installing, using, and checking the standard calorimeter is to be prescribed by the London Gas Referees.

(4) That, subject to the acceptance by the gas undertaking of the stipulations laid down in articles Nos. 1, 2, 3, 5, 6, and 7, the gas undertaking is to be free to deliver to the consumer any mixture of combustible gases free from sulphuretted hydrogen, and not containing more than 20% of inert constituents for two years, 18% for two years thereafter, and 15% thereafter.

(5) The gas undertaking to declare the calorific value of the gas it

intends to deliver, and to undertake to adjust, and if need be to replace gratis, the burners in consumers' appliances, with all reasonable speed, so that the gas delivered can be burned in these appliances with safety and efficiency

(6) Should the gas undertaking desire at any time to change the calorific value of the gas supply, due notice to be given to the consumers or their representatives. During the period of notice, preparations to be made by the gas undertaking for any readjustment of the consumers' appliances which may be required, so that the gas then to be delivered can be burned in these appliances with safety and efficiency.

.7) The gas undertaking, within a period of five years, to supply gas at such pressure that, under normal conditions of supply and equipment, there shall be a pressure of not less than 20-10ths of an inch of water on the gas in any main or service-pipe of 2 in. diameter and upwards.

(8) That the unit to be adopted in charging the consumer is to be 100,000 B.Th.U.

The Fuel Economy Committee [15] of the British Association in presenting their Annual Report express general agreement with the soundness of supplying gas on the basis of its heat value, and with the recommendations of the Fuel Research Board subject to certain conditions being assured. They are of the opinion that insufficient importance has been attached to the value of methane as a " steadying " constituent of the flame produced by the combustion of coal gas, and suggested that the proportion of this constituent should not fall below 20%. They further advocate the limitation of the quantity of carbon monoxide present in coal gas owing to the toxic effect produced in the event of small leakages, and recommend that a maximum value of 20% of carbon monoxide should be instituted

The work that has been carried out at Leeds University is of immense value in indicating the general lines of future progress in the industry, but the investigators have recognised that much has yet to be done before an absolute decision can be arrived at concerning the future standards of gas supply. Future research should probably lie in the direction of investigating the question fundamentally, which would involve the determination of values for each of the constituents of coal gas studied first separately, and then in varying proportions. Insufficient is known at present about the effect of each constituent in determining flame temperature and structure, radiation efficiency, and the rate of propagation of explosive wave with varying gases and appliances used with different proportions of air.

R. V. Wheeler [46] has shown that methane and air mixtures containing

[15] *Iron and Coal Trades' Rev.*, Sept. 12, 1919, 327 ; *J.*, 1919, 355A.

[46] *Chem. Soc. Trans.*, 1918, 113, 840 ; *J.*, 1919, 34.

from 7·5 to 12·5% of methane inflame in such a manner that the flame reaches simultaneously all points of the walls of the containing vessel. In consequence the inflammation is complete before cooling by conduction from the walls comes into play. Mixtures containing more than 12·5% or less than 7·5% of methane inflame so that cooling by conduction can take place before the combustion is completed, and consequently the maximum pressure in this case is less than in the former.

The same author also finds [47] that the speed at which flame is propagated through an inflammable mixture is dependent upon the degree of mechanical agitation of the mixture. The rapidity of combustion increases with the degree of turbulence, and a mixture in which the speed of flame is normally slow is more affected by turbulence than one in which the normal speed is high. The lower limits of inflammability of various mixtures of hydrogen, methane, and carbon monoxide in air together with that of " town's gas " and air, have been determined by H. F. Coward, C. W. Carpenter, and W. Payman.[48] The results obtained show that the lower limits for the various mixtures may be calculated with fair accuracy from Le Chatelier's formula, in which n_1, n_2, n_3 . . . are the proportions of the several combustible gases in the lower limit mixture expressed in percentages of the total gas mixture, and N_1, N_2, N_3 . . . are the corresponding percentages for each of the combustible gases taken separately, then :—

$$n_1/N_1 + n_2/N_2 + n_3/N_3 + . . . = 1.$$

The upper limits in air saturated with water vapour at 18°–19° C. are found to be approximately 74·2% for hydrogen, 15·4% for methane, and 74·2% for carbon monoxide. The upper limits for mixtures of these gases and also the upper limit of coal gas can be calculated approximately from the above formula.

W. Payman and R. V. Wheeler [49] find that small variations in the composition of a combustible gas have a considerable effect on the speed of flame propagation. A reduction in the proportion of paraffins and an increase in the proportion of hydrogen, which occur when carburetted water-gas is employed to dilute coal-gas, must inevitably increase the speed of flame propagation in the air mixture. Such works as these clearly emphasise the importance of composition as a factor in determining the suitability of gaseous mixtures for commercial purposes and the need for further research along these lines.

The position of the coal gas industry in relation to fuel consumption has been examined very carefully by D. Clerk, A. Smithells, and J. W. Cobb [50] at the instigation of the Institution of Gas Engineers. They

[17] *Chem. Soc. Trans.*, 1919, **115**, 81 ; *J.*, 1919, 127A.
[48] *Chem. Soc. Trans.*, 1919, **115**, 27 · *J.*, 1919, 126A.
[19] *Chem. Soc. Trans.*, 1919, **115**, 36 ; *J.*, 1919, 126A.
[50] *Gas World*, **70**, 333.

have worked out detailed comparisons with the electricity supply industry in order that the question from the point of view of conservation of coal may be appreciated. These comparisons show that for heating purposes the thermal efficiency of the gas-making process is very much superior to that of the generation of electricity, whilst this superiority is not so pronounced in the case of lighting and power. The report is a lengthy one, and many factors have to be considered in arriving at the basis upon which comparisons shall be made. For instance, the determination of the thermal efficiency of the carbonisation process is naturally based upon the assumption that the products, namely, gas, coke, tar, ammonia, sulphur, etc., be included as heat-containing bodies. On this basis an average of about 71% of the total heat of the coal is conserved on carbonisation, this appearing in the products, the remaining 29% being employed in the process of manufacture. The reporters are strongly of the opinion that the maintenance and development of the gas industry are essential in the interest of fuel conservation.

MINERAL OILS.

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PETROLEUM AND THE WAR.

IT is a truism to state that the Allies' success in the European War was largely due to the supply and utilisation of petroleum. Certainly, without mineral oil warfare would have remained in a mediæval condition and an impasse might have resulted. It is scarcely possible at this date to imagine strategy and tactics deprived of tanks, aircraft, motor transport, and oil-fired ships, whilst industry on the home front lacked a variety of essential petroleum products such as fuel for internal-combustion engines and lubricating oils for machinery.

Some idea of the vital importance of the reaction of petroleum on the great struggle may be obtained from a perusal of the speeches at the Annual Dinner of the Institution of Petroleum Technologists.[1] Lord Moulton referred to the importance of Borneo spirit as a source of toluol and to the various attempts which had been made to " constructively distil " paraffinoid and saturated cyclic hydrocarbons into aromatic derivatives. Sir Charles Greenway, the retiring President, emphasised the need of continuous study and research and training in the technology of petroleum—and in connection with this reference may be made to the munificent gift made by the Anglo-Persian, Burmah, and Anglo-Saxon Companies and Lord Cowdray, the Hon Clive Pearson, and Mr. Deterding to the Chemical School at Cambridge

Sir Frederick Black, the incoming President, made the first reference to the pipe line (32 miles in length) between the Clyde and the Forth. which would have proved of the greatest benefit had the war continued. He drew attention to the fact that the stupendous total of 30 million tons of oil was moved into European waters during the war (as against 240 million tons of coal moved out of the United Kingdom), and emphasised the work of the Anglo-Persian Oil Co. in supplying the whole of the Mediterranean area with oil, and the Asiatic Petroleum Co.'s efforts in connection with toluol for explosives. The Fourth Sea Lord (Admiral Sir H. Tothill) spoke appreciatively of the value of oil fuel and the carriage of fuel in double bottoms, no less than one million tons being brought over the Atlantic in this way.

[1] *J. Inst. Pet. Tech.*, 1919, 5, 221 *seq.*

On a later occasion Sir Frederick Black in his Presidential Address [2] made further reference to the all-important work of the great oil companies, instancing the Shell Group's efforts in the direction of explosive supply, in distribution of service motor spirit and in the fitting up of the double bottoms of cargo ships for supplementing oil transport, whilst the Anglo-Persian Company satisfied most of the Mediterranean supply and rendered invaluable service in connection with the Mesopotamian expedition. The main problems that confronted the Allies were: (1) whether the world could produce the aggregate supplies that were required for the service of the war, (2) whether the processes of refining could be so adjusted that the increased quantities of heavy fuel could be obtained as well as those of petrol, particularly of the high grade required for aviation purposes; (3) whether sufficient tankers, cars and receptacles could be provided to transport and distribute by sea and land the necessary quantities of each product. That these problems were satisfactorily solved reflects the greatest credit on those concerned.

A vast amount of persistent investigation and research was set in motion throughout the war, and it is not too much to say that a wider and deeper knowledge of the chemistry of petroleum is one of the good results of the struggle.

The Burmah Oil Company did a very considerable amount of most important and valuable work, not only for the Eastern campaigns and the situation in India generally, but also in connection with supplies of aviation and motor spirit for Great Britain and her Allies in Europe, and at a time when the situation with regard to tonnage was so acute, practically bore the whole brunt of keeping the huge Indian market supplied with its essential requirements of illuminating oil, batching oil, lubricants, and petroleum spirits.

The Anglo-Persian Oil Company's efforts were largely bound up with the supply of petroleum products to the M.E.F. and to the Navy. The benzine and kerosene topped from the crude during the production of Admiralty fuel oil was distributed mainly in the East and the Mediterranean, thus diverting American supplies to a nearer route. Owing to the strategic importance of the Company's Persian refineries, the Mesopotamian campaign was provided with an indigenous supply of all petroleum products, ranging from aviation spirit, petrol, and burning oil to fuel oil. If these supplies had not been available on the spot, the strain on supplies from other sources and upon the limited tank-steamer tonnage would have been greatly intensified and the cost of the M.E.F. campaign have been vastly increased. Investigations during the war showed that the benzine was, in itself, a valuable source of toluol, the concentration amounting to about 5%, whilst a readily-prepared concentrate of 10% could be shipped direct from the refinery.

[2] *J. Inst. Pet. Tech.*, 1919, **5**, 251.

From this material further fractionation gave a 30% toluol content which was nitratable, and from which T.N.T. was made on a working scale. This discovery is naturally of first importance in the Middle East and in India.

A considerable amount of work was done in connection with the cracking of petroleum distillate to a rich toluol concentrate, although the heavy conversion losses, due to operating at a high temperature, and the increased production of toluol from other sources prevented this process from being an economic success so long as there was no ready market for the large proportion of uncondensable gases. Similar considerations played a corresponding part with analogous attempts in America.

Production of Aromatic Hydrocarbons from Persian Heavy Distillate.

	Per cent.
Throughput of 45% dist. from Persian fuel oil	—
Toluene spirit made	21·84
Residues	26·34
Losses in tanks	0·77
Conversion losses, gas, and coke	51·05

The average spirit produced gave the following results :

	Percentage in spirit	Percentage on original crude
Benzene	17·1	3·73
Toluene	16·5	3·60
Xylenes	5·7	1·25

In their own particular spheres important service was rendered by the Scottish shale companies, which produced annually 300,000 tons of refined oils, and the Trinidad companies which contributed fuel oil, benzine, and kerosene, whilst the bulk of the necessary cargoes, both for refined and fuel oils, was necessarily provided by the American and Mexican fields.

The Commercial Extraction of Aromatic Hydrocarbons from Petroleum during the War.

As is well known, certain crude petroleums contain varying percentages of aromatic hydrocarbons, those of some Bornean and the Persian fields being particularly noticeable in this respect. The coal tar and gas industries were quite unable to meet the unprecedented demand for toluene for T.N.T. manufacture, but fortunately the Asiatic Petroleum Company, which possessed not only the necessary aromatic-rich petroleum, but also the plant for working it up, was able to provide the necessary supplies.

Toluene from Petroleum.

So long ago as 1907 the late H. O. Jones, of Cambridge, isolated

toluene from Borneo petroleum,[3] and it appears to be well authenticated that derivatives of this hydrocarbon were actually in use on this Continent long before the war.

The toluene produced from petroleum is of great purity, being uncontaminated by any sulphur or oxidisible compounds. As manufacturers of nitrotoluene usually object to the presence of paraffin hydrocarbons in the toluene, and as it is obviously impracticable to manufacture pure toluene from a mixture of this with hydrocarbons of other series, another method of manufacture of the nitrotoluene was adopted. In the first place, a fraction rich in toluene (60%) was prepared by the careful fractionation of the benzine from certain Borneo crudes. This fraction contained 40% of other hydrocarbons, but no benzene or xylenes. The preparation of such a fraction was not a very difficult matter, about 90% of the toluene present in the benzine being concentrated into this fraction. This fraction was then nitrated, and the resulting mixture of mononitrotoluene and hydrocarbons was separated by fractional distillation. A pure mononitrotoluene was thus obtained, which by further nitration was converted into the trinitro compound. In a similar way quantities of nitration products of xylol were made.

ESTIMATION OF TOLUENE IN PETROLEUM.

Various methods for the estimation of the toluene content of petroleum have been devised.

F. L. Thole [1] summarises previous methods for the determination of aromatic hydrocarbons, in particular the sulphur dioxide method, and derives an excellent and accurate assay by means of density determinations before and after the petrol has been extracted with thrice its volume of 98% sulphuric acid, seeing that few straight-run petrols contain olefines and that acid of the specified strength has negligible action on naphthenes or paraffins. Correction must be made for the non-additive density relationship in mixtures of aromatic and aliphatic hydrocarbons, and this may be done by means of a curve.

H. G. Colman and E. W. Yeoman [5] determined the deviation correction, confirming Thole's values and carrying the determination further by including xylene.

J. Tausz and A. Stuber [6] separated toluene and xylene from Roumanian petroleum by solution in liquid sulphur dioxide at comparatively low temperatures (-80° and -15° C. respectively) The sulphur dioxide extract was repeatedly extracted with light petroleum, previously chilled to the same temperature, and in this way substantially the whole bulk of the aromatic hydrocarbon was recovered relatively free from paraffins and naphthenes.

[3] *Chem. Soc. Trans.*, 1907, **81**, 1146.   [1] *J.*, 1919, 39T.   *J.*, 1919, 82T.
[6] *Z. angew. Chem.*, 1919, **32**, 175; *J.*, 1919, 524A.

INDIGENOUS FUEL OIL.

The Mineral Oil Production Department carried out lengthy tests on the possibility of producing fuel oil from cannels,[7] and it was decided to utilise the plant and the trained staff of the gas works for this purpose. At one installation 100 tons of cannel was treated daily in vertical retorts with an output of crude oil of 4000 gallons. The oil is brownish-black in colour and possesses a characteristic odour. The specific gravity is about 0·930, the oil is mobile but possesses a sharp setting point, due to its considerable wax content. It mixes readily with mineral fuel oil and may be employed directly under boilers or in Diesel engines. Reference has been made in previous Reports to the cannel oil question generally and to the recommendation of the Institution of Petroleum Technologists' Committee, and although in point of fact, the actual contribution of fuel oil to the Service was almost negligible compared with that imported from the United States, yet useful pioneering work was done which will bear fruit ultimately in the production of a notable volume of insular oil. In this direction, attention may be drawn to a monograph which owes its origin to the efforts of the committee referred to [8]

FLAME PROJECTORS.

The German *Flammenwerfer* consisted of a cylindrical vessel of steel, two feet long and 15 inches in diameter, arranged to be strapped on the back of the operator [9] Two-thirds of the way up was a filling hole for oil, near the top a pressure gauge, and towards the base a cock to which was attached a flexible hose ending in a nozzle. Internally the cylinder was divided into two compartments, the upper of which held nitrogen at a pressure of 23 atmospheres, and the lower contained oil. The inflammable material contained light and heavy components carefully proportioned, and the former material, which ensured the keeping alight of the jet. was originally light gasoline and later ether. When the oil under pressure is forced out of the jet it moves a friction lighter which ignites a core of a fierce-burning fuse mixture.

HELIUM FOR AIRCRAFT

Helium in natural gas was suggested in the first place by Sir **W.** Ramsay (Feb. 1915), and investigations instituted in the United States showed that the isolation of this gas was practicable.[10] By the time of the signing of the armistice no less than 147,000 cub. feet of helium was in dock ready for shipment. The value of a non-inflammable

⁷ See also *Ann. Repts.*, 1918, **3**, 80–82.
⁸ "*British Oil Industry*," W. R. Ormandy, F. M. Perkin, A. Campbell, A. E. Dunstan, and A. H. Seabrook; Griffin & Co., 1919.
⁹ S. J. M. Auld, *Gas and Flame*, New York, 1918.
¹⁰ See F. G. Cottrell, *J.*, 1919, 122т.

gas with great lifting power is obvious from the point of view of air-craft, both in war and peace.

PRODUCTION OF OIL FROM MINERAL SOURCES.

The Committee appointed by the Institution of Petroleum Tech-nologists presented its final report in April last,[11] and it is stated that as the outcome of the interim report of August, 1918, a com-pany has been formed to produce oil from bituminous material. It is anticipated that the company will fulfil a useful function in inves-tigating new types of retorts and in determining the most profitable use and method of treatment of any particular retortable material.

A discussion of the whole of this problem is given by F. M. Perkin,[12] in which comparison is made between the products of high and low temperature carbonisation, and a comprehensive survey is made of the oils derived from Scottish shale, Kimmeridge shale, peat, and lignite. In connection with the latter mineral, it is claimed that, after conver-sion into producer gas, electric power may be generated at 0·06 of a penny per B.T.U. Perkin criticises the Munitions Mineral Oil Produc-tion Department for desiring yields of fuel oil from the steaming of charges in gas works on the grounds that the best use of the plant obviously lay in production of the usual aromatic by-products, whereas low temperature carbonisation could have supplied part of the needs for fuel oil. By the steaming process there was obtained only 1,845,000 gallons at a cost of 1s per gallon The chief low-temperature plants are briefly described In the discussion Ormandy described the pro-cedure at the lignite works near Teplitz, where the carbonised material was briquetted by the residue from the tar. He drew attention to the lignite deposits in Wernsburg, where also was found clay of the highest quality.

S. R. Illingworth [13] gives particulars of a mineral oil obtained from the retorting of a shale. Yields of 31 and 18 gallons per ton were pro-duced from two materials and satisfactory percentages of naphtha, kerosene, fuel oil, and wax were contained therein

A thoughtful discussion on American oil shales and their potentiali-ties is contributed by R. F. Bacon and W. A. Hamor.[14] It is pointed out that in Colorado alone there is sufficient retortable material to yield 20,000,000,000 gallons of crude oil whilst in Utah an equal quantity is available.

English Oil Fields, Ltd., has made considerable progress in Norfolk.[15] Nineteen bore holes have been sunk and evidence of the thickness of the shale seams has been obtained, no less than 150 feet of retortable

[11] See J., 1919, 149R.
[12] J. Inst Pet. Tech, 1919, 5, 75; J., 1919, 401A
[13] J., 1919, 355T.
[14] J., 1919, 161T.
[15] J., 1919, 337R.

material having been pierced. Some of the borings passed through 70 feet of a material which is said to yield a large percentage of wax. The oil from the middle shales is alleged to be of good quality and to be practically free from sulphur. Adjoining the property are chalk and clay, and it is proposed to utilise surplus gas production for cement manufacture. For the occurrence of sulphur in Norfolk shale oil reference should be made to a paper by W. Forbes-Leslie.[16]

English Petroleum.

So long ago as 1896 the late Sir Boverton Redwood suggested that oil might be found in England on a workable scale, and advocated on many occasions that the ultimate test of the drill should be applied. In 1911, after examining the oil found at Kelham, he stated that a true normal petroleum had been struck and in 1914 he urged that the bore should be deepened, believing that more productive strata might be found at greater depth. It is therefore a strange coincidence that his last official work lay in the examination of the Hardstoft crude.

It is of interest to remember that the flow of oil at the Riddings Colliery, Alfreton, led to the establishment of the Scottish shale oil industry by James Young, who between 1847 and 1850 actually refined the oil, and produced kerosene, lubricating oil, and wax therefrom.

The exploration of England for petroleum was first instituted by the Mineral Oil Production Department ; that duty has recently been transferred to the Petroleum Executive, the Director of which is Sir John Cadman. The actual operations are being conducted by Messrs. S. Pearson and Son, Ltd. Eleven drilling sites were selected, seven in Derbyshire, two in North Staffs, and two in Midlothian. The Hardstoft well was spudded in on October 15, 1918, and at a depth of 3077 feet oil was struck on May 27, 1919.[17] The encouraging results thus obtained were largely due to the geological work of Dr. A. C. Veatch and to Mr. J. E. Hackford's chemical investigations. The latter observer had so far back as 1915 forecasted very closely, from the evidence at his disposal, the probable composition and products of the English oil. The actual analysis made by Mr. J. E. Hackford of the Hardstoft oil is :—

Specific gravity			0·823
Flash point (Abel closed)			35° F.
Setting point			0° F.
Viscosity, Redwood 1. at 32° F.			212 secs.
,, ,, ,, 40° F.			157 ,,
,, ,, ,, 60° F.			74 ,,
,, ,, ,, 80° F.			57 ,,
,, ,, ,, 100° F.			48 ,

[16] J. Inst. Pet. Tech., 1916, 3, 3 ; J., 1917, 204.
[17] See J., 1919, 201 B.

Viscosity, Engler at $20°$ C. . . . . 113 secs
,, ,, ,, $40°$ C. . . . 81 ,,
,, ,, ,, $60°$ C . . . . . 71 ,,
Sulphur . . . . 0·26%
Ash . . . . 0·036%
Wax (m. pt. $104°$ F.) . . . . . 0·25%
Calorific value . . . . 20,290 B.Th.U.

Products from Hardstoft Oil.

Motor Spirit.— Numerous distillation tests under various conditions were undertaken, from which it is ascertained that there can be produced commercially from this oil the following : Aviation spirit, 4·5% ; first grade commercial spirit, 7·2% ; commercial motor spirit, 10·0% ; total, 21·7%. The aviation spirit has sp. gr. only 0 689 at $60°$ F. and complies with specifications.

Kerosene, Lamp Oil, or Burning Oil. The kerosene, lamp oil, or burning oil obtained, varies in percentage from 30 to 40%, according to the quality it is desired to obtain. Both qualities, however, are exceptionally good, and an analysis of kerosene representing 33% of the crude is Sp gr at $60°$ F, 0·783 : flash point (Abel closed), $135°$ F. ; flash point (Abel open), $151°$ F. ; fire test, $161°$ F. ; colour (Lovibond's petroleum standard 18-in cell), water-white ; sulphur, 0·08%.

Gas Oil.— Gas oil suitable for forming the basis of fuel oils, or for gas-producing in gas works, is obtained of excellent quality

Lubricating Oils. The heavy lubricating oil obtained (30%) is so satisfactory in character and quality that it compares to advantage with any of the best Pennsylvanian products. It has : Sp gr at $60°$ F., 0·893 : flash point. closed P M., $514°$ F. : flash point. open, $554°$ F ; fire test. $596°$ F. , setting point, $35°$ F ; viscosity, R I. at $100°$ F., 3736 secs ; $140°$ F., 1077 secs ; $180°$ F., 328 secs. ; $200°$ F , 218 secs. ; $212°$ F., 172 secs , ash, 0·01%.

The flow of oil is estimated at about 400 gallons per day. A show of oil was found in the Ironville No. 1. well at 2022 feet and in Ironville II. well at 2170, 2640 and 3029 feet.

Towards the middle of 1919 a license to drill on the Kelham estate was granted to The Oilfields of England. Ltd. The enterprise is not exactly new, for a syndicate struck oil at Kelham on August 21, 1911, at 2440 feet. The Kelham oil is heavier than that found in Derbyshire, and on being topped, it yielded 91·4% of fuel oil, of Admiralty specification.

Petroleum from other Sources.

Papua.— J. Read and M. M. Williams [18] describe the results of an examination of two samples of oil from Papua. The Vailala crude oil was light brownish-yellow with blue fluorescence and resembled Borneo

[18] *J.*, 1919, 319т.

oil. It had sp. gr. 0·796 at 18·75° C.; 37% (wt. wt.) of naphtha
boiling below 170° C., of sp. gr. 0·711, was obtained. The fraction
60°-90° C. contained 7% of benzene, and the sp. gr. of the unnitrated
oil pointed to the presence of naphthenes There was 10% of toluene
in the 90°-120° fraction and 13% of xylenes, etc., in the 120°–150° cut.
These facts lend considerable interest to the oil as a source of toluene.

   Mesopotamia.—A belt between Kirkuk and Bagdad is oil-bearing in
parts. There are also oil shows on the Middle Tigris and on the
Euphrates south of Hit.[19]

   Alsace.—At the outbreak of war developments were in progress for
a production of 70,000 tons of oil per annum The oil is struck at
650-1650 feet, and is accompanied by very saline water. Chemically
the oil is intermediate in character between American and Roumanian
oils and has an average sp. gr. of 0·92. It yields 5% of petrol and 29%
of kerosene, and leaves a pitch residue of 10%[20]

Statistics

   Important data were given by Sir Charles Greenway in discussing
Ormandy's paper on motor fuel.[21] The use of kerosene in Great Britain
for motor fuel purposes reached 200,000 tons per annum in 1918, and is
estimated at 400,000 tons in the near future, a quantity equal to the
whole pre-war consumption of benzine The world's production of crude
petroleum for 1917 was more than 70,000,000 tons, and would have
been very much greater had it not been for difficulties experienced in
obtaining drilling and refining plant and tonnage owing to war condi-
tions. As an example, the Persian production of 1,030,000 tons in 1917
would have been in the neighbourhood of 5,000,000 under more favour-
able circumstances, yielding thrice the total pre-war benzine consump-
tion of the United Kingdom. The speaker considered that there was
at present no risk of serious shortage of straight-run benzine, and that
the cracking of heavy oils would, when necessary, be the most promising
means of supplying the deficiency During the same discussion, Mr.
T. C Thomson remarked that of the wells sunk in Mexico but at present
shut down, the production would equal half the present-day production
in the United States, whilst it is estimated that the ultimate expected
production will equal, if not surpass, the whole production of the United
States. The production of casing-head gasoline in the United States
amounts to approximately 10% of the total straight-run benzine, and
a much greater amount could be obtained from the great volume of
natural gas which is produced.

   M. Summers [22] quotes the 1917 production as 503,708,000 barrels,

[19] *J.*, 1919, 47R.
[20] *Rev. Gen. d'Elect.*, Aug. 23, 1919 ; *J.*, 1919, 377R.
[21] *J. Inst. Pet. Tech.*, 1918, **5**, 56.
[22] *J. Inst. Pet. Tech.*, 1918, **5**, 148.

and gives the British capital invested in oil as £125,000,000, whilst the corresponding American figure is £380,000,000. £20,558,558 of British capital is invested in Mexico, where, in 1917, 55,292,770 barrels were produced.

C. C. Smith,[23] in an interesting survey of the genesis of the American Petroleum Institute, points out that in the year 1917, 886 casing-head gasoline plants were in operation in the United States, producing 217,881,101 gallons of spirit from an average yield of half a gallon per 1000 cubic feet. He disclosed the fact that 18% of the power used by the British Navy was derived from petroleum, and that the fleet steamed 7 million miles per month. In 1918 three million tons of fuel oil was shipped from the States to the Allied Navies, together with one million tons of other petroleum products. Illustrating the enormous demand for gasoline, he instances the estimated total of petrol-driven cars in the United States to be seven million, i.e. a car for one family in every four.

THE STANDARDISATION OF PETROLEUM TESTING.

Reference should be made to a valuable contribution to this subject by A. Philip.[24] The author considers that it is not practicable to issue standard test samples, as is the case for the iron and steel industry, but prefers to have laid down the most precise and detailed instructions for the carrying out of the various operations involved. A considerable body of investigations already exists, owing to the activity, amongst others, of the Bureau of Mines in America and our own National Physical Laboratory. What is now needed is the welding of these researches into a comprehensive whole by some international or inter-allied commission, which, sitting permanently, shall institute enquiries into new methods of procedure and revise existing technique.

NATURAL GAS

Attention has already been drawn to the isolation of helium from American natural gas, and to statistics relating to the production of casing-head gasoline. A considerable amount of work has been carried out from the standpoint of hydrocarbons as a starting-out point for synthetic chemical industry. Preliminary experiments have shown the practicability of the commercial chlorination of natural gas, which is largely composed of methane. Methyl chloride and carbon tetrachloride, widely in demand for fire-extinguishing appliances, are both important derivatives. Specially activated charcoal appears to be the best catalyst for the chlorination of natural gas, and the effect of catalysts in general is discussed by R. V. Kokatnur.[25]

W. P. Dykema [26] points out that if the sp. gr. of the crude oil is less

[23] Gas Age, 1919, 44, 90.
[24] Inst. Pet. Tech. Oct. 21, 1919; J., 1919, 939A.
[25] J. Amer. Chem. Soc., 1919, 41, 120; J., 1919, 199A.
[26] U. S. Bureau of Mines, Bull. 151, 1918; J., 1919, 99A

than 0·920 the gas can be profitably treated for recovery.   Most casing-head gasoline is blended with about an equal bulk of naphtha, *i.e.* the fraction removed after the straight-run gasoline has been distilled.

G. W. Jones and V. C. Allison [27] pass natural gas rich in methane with a slight excess of chlorine through a tube which contains a suitable catalyst, heated in an electric furnace. Suitable contact agents are gas-mask charcoal and steamed anthracite coal, both of which have a high absorptive capacity for chlorine. The reaction begins at 250° and increases in intensity to 500° C., beyond which the charcoal is attacked. Methane and ethane may be completely chlorinated by selecting a suitable rate for the gas mixture, whilst by increasing the gas velocity chloroform also is produced.

On the same lines, the attack on petroleum as a basis for synthetic chemistry, should be noticed the patent of G. G. Oberfell and H. L. Boyd,[28] in which chloro-paraffins are converted into acetic esters by treatment with an alkali acetate and acetic acid in presence of an alkali sulphate.

THE COMPONENTS OF BENZINE.

Although the determination of the olefinic, the sulphur, and the aromatic content of benzine is comparatively simple, hitherto there has been no clearly defined way of estimating the relative proportions of paraffinoid and cyclo-paraffinoid hydrocarbons. The investigations of C. Chavanne and L. J. Simon [29] appear to fill this gap. The fundamental observation is that paraffins and cycloparaffins have different critical solution temperatures in aniline   For example, in the former case the C.S.T. varies from 71° to 69° C., whilst in the latter it is from 10° to 49°, the hydrocarbons varying from C_5 to C_8. Some interesting analyses are quoted of Borneo, Sumatra, and Persian benzines, the results of which, however, await confirmation. An example will illustrate the claims :—

	Persian I. %	Persian II. %
Benzene	2·31	1·0
Toluene	2·55	4·0
Xylene	0·65	6·0
Higher aromatic hydrocarbons . .	—	2·7
Cyclopentane	0·6	—
Methylcyclopentane	6·2	2
Cyclohexane	1·7	1·5
Methylcyclohexane	6·4	4·0
Dimethylcyclohexane	3·3	5·0

[27] *J. Ind. Eng. Chem.*, 1919, 11, 639 ; *J.*, 1919, 599A.
[28] U.S. Pat. 1302583 ; *J.*, 1919, 554A.
[29] *Comptes rend.*, 1919, 168, 1111 ; 169, 70, 185, 285 ; *J.*, 1919, 619A, 672A

Evidently the method depends very considerably on the efficacy of the fractionation.

Chavanne and Simon determine the aromatic content in petroleum spirit by observation of the critical temperature of solution in aniline before and after removal of the benzenoid hydrocarbons. The two temperatures being represented by T_1 and T_2 the aromatic content is given by $A_2 = K (T_2 - T_1)$. When A_2 is not greater than 15 20%, $K = 1.18$. Various corrections are made for olefines and traces of nitro-compounds left in the spirit and for slight departures from the additive law.

A mixture of two acyclic hydrocarbons or a mixture of one acyclic and one saturated cyclic hydrocarbon obeys the additive law so far as the C.S.T. in aniline is concerned, but a mixture of two saturated cyclic hydrocarbons does not obey this law. The addition of an aromatic hydrocarbon to non-aromatic hydrocarbons results in a depression of the C.S.T. proportional to the amount of aromatic hydrocarbon added.

The same method is available for the determination of naphthenes in the presence of paraffins, but the petroleum should be so fractionated that only one saturated cyclic hydrocarbon is contained in the fraction under examination. In this case after the removal of the aromatic compounds the estimation simply becomes a determination of the C.S.T.

In general the results may be obtained from the following expressions, in which the contents have been empirically evaluated :- -

Aromatic content $(Ar) = 1.18 (T_2 - T_1)$

Cycloparaffins $(C) = \dfrac{72 - (T_2 + 0.2)}{32.5} (100 - Ar)$.

Alicyclic hydrocarbons $= 100 - Ar - C$.

If olefines are present the value T_1 must be expressed as $T_1 + 0.4 E$, where E is the percentage of olefines in terms of amylene.

BENZINE.

The evaporation velocity of motor fuels has been determined by K. Dieterich.[30] Light, medium, and heavy benzines, benzol, and alcohol have been investigated. A short, steep, straight curve indicates the best quality of fuel, whilst a long, irregular curve is characteristic of a fuel containing a high proportion of less volatile components.

H. Wegrzyn [31] has studied the action of the Grignard reagent on halogenated benzine fractions of Boryslaw crude oil. The brown derivatives gave no fatty acid, but the chloro-compound of fraction 80°-156° C. gave a 40% yield of a mixture of carboxylic acids, chief amongst which it is alleged occurs hexanaphthenecarboxylic acid, $C_6H_{11}CO_2H$. Wholly unsuccessful attempts were made to obtain acids from solid

[30] *Petroleum*, 1917, 12, 676; *J.*, 1919, 244A.
[31] *Petroleum*, 1918, 13, 241; *J.*, 1919, 278A.

FUEL OILS.

F. Tinker [39] finds that stable mixtures of pitch-containing tars with mineral oil may be produced by means of an oil intermediate in respect to chemical composition and surface tension. The intermediary oil may be an asphaltic residuum or an oil rich in aromatic components or a " blown " shale oil. Approximately equal proportions of the three constituents are used. In an addition to his patent he makes the claim that the more complete stabilisation of the mixture may be effected by the incorporation of alkali, insufficient to neutralise the total content of organic acid present in the oil ; the addition of 0·5% of 10% aqueous ammonia is a suitable amount in most cases.

Reduction of viscosity of mineral oils or residues may be accomplished by heating to 360° 420° C under 4–6 atmospheres pressure. [40] An alteration in the molecular condition is claimed without any further thermal decomposition.

ASPHALTS.

5. Marcusson has contributed in the past very materially to the highly involved chemistry of this complex subject. Two papers may be noticed. [41] The asphaltogenic acids in natural asphalts are brown tarry matters containing considerable amounts of sulphur. They form sparingly soluble sodium salts and on prolonged heating form anhydrides. At high temperatures they are converted into substances which resemble asphaltenes.

The bituminous components of natural and artificial asphalts, insoluble in petroleum ether (asphaltenes), resemble coal in their behaviour to reagents ; they contain rather less nitrogen and more hydrogen, but are, unlike coal, soluble in benzene and carbon tetrachloride. The carbenes which occur in grahamite are insoluble in carbon tetrachloride and also resemble coal. Albertite, which represents a further stage in inspissation, is insoluble in organic solvents, and the name " carboid " is suggested for such substances. The resemblance in the behaviour of coal and asphaltic substances must be ascribed to the common possession of polycyclic structure and similarly linked oxygen.

REFINERY TECHNIQUE.

Reference should be made to the appearance of the first British monograph on this subject by A. Campbell. [42] The author was for many years the manager of the Burma Oil Company's refinery in Rangoon and writes with authority on a subject which has attracted singularly little

[39] Eng. Pats. 130699 and 132960 ; J., 1919, 711A, 856A.

[40] Allgem. Ges. f. Chem. Ind., Ger. Pat. 308197 : J., 1919, 5A.

[41] Chem.-Zeit., 1918, 42, 437 ; J., 1919. 98A. Mitt. k. Materialpruf., 1918, 36, 209 ; J., 1919, 453A.

[42] C. Griffin & Co., London, 1919.

attention. This state of affairs, however, is likely to be remedied in view
of the establishment of the Anglo-Persian Oil Company's refinery at
Swansea and the developments which are imminent in other directions.
At the inaugural ceremony in May of this year, the Chairman of the
Company, Sir Charles Greenway, in explaining the reason for the refin-
ing of crude oil in this country, made the happy comparison that the
tanker which brings in the oil may be regarded as an extension of the
pipe line from the fields to the seaboard.

Bulletin 170 on Oil and Gas Fires (Petroleum Technology, Bureau
of Mines) [13] discusses at length the foam method of extinguishing oil
fires, and the importance of the subject is borne out by the fact that
during the years 1908-1918, 12,850,000 barrels of oil and 5,024,506,000
cubic feet of gas were destroyed, involving a loss of $25,252,200. Small
gasoline fires are best extinguished by means of mixtures of sawdust and
sodium bicarbonate containing 8 lb. of the salt to 1 cubic foot of saw-
dust.

Writing on the present state of refinery practice, E. W. Dean [41] dis-
cusses the urgency of permitting a higher final boiling point for gasoline
and suggests 230° C., thereby increasing the available supplies by
15 20%. Greater efficiency in fractionation would bring about a
further 10% increase in yield.

The application of the sodium plumbite method of desulphurising
oils is described by S. Schwertz and H. G. Nevitt.[15] The following
sulphur contents are given : Appalachian, 0.05 0.08% ; Lima, Ohio,
0.3 0.5% ; California, 1.0% ; Mid-Continental, 1.046 1.3% ; Texas,
2.0-3.0% ; Mexico, 3.0-4.0%.

The statement [46] that the Badische Anilin und Soda-Fabrik has
taken the initial steps in the production of synthetic mineral oil, pos-
sibly relates to the reduction process of Bergius in which, under very
high pressure, hydrogen may be added to unsaturated hydrocarbons
and even to coal substance.

Dealing with the perennial subject of the oily constituents of acid
tar, S. Gasiorowski and G. v. Kozicki [17] obtained by steam distilla-
tion of an acid tar, an oil of sp. gr. 0.9685 at 18 C., which was entirely
soluble in liquid sulphur dioxide, thus showing that the effect of refining
by sulphuric acid is to remove unsaturated compounds. Reference
should be made to the work of B. T. Brooks and J. Humphrey.[48]

[43] J., 1919, 327R.
[44] Oil and Gas J., 1919, 17, 52.
[45] Petroleum (Chicago), 1919, 7.
[46] J., 1919, 9R.
[47] Bergbau u. Hutte, 1918, 4, 181 : J., 1919, 35A.
[48] J. Amer. Chem. Soc., 1918, 40, 822; J., 1918, 361A. Ann. Repts., 1918,
3, 64.

CRACKING.

The volume of patent applications in this field shows no signs of diminution and the number of permutations and combinations of the variables is apparently almost infinite. There is no modification of outstanding novelty which can be quoted.

The most important communication on the subject is by O. Aschan,[19] who has written a valuable summary of the commercial aspects of cracking Russian residuum or masut. At the present time, after topping, Russian crude leaves a residue of which 10% is worked up for fully refined products and the remainder is used as fuel oil. The effect of refining is to double the price referred to the crude oil. Seeing, however, that the market can only absorb a limited amount of refined material, the possibilities of cracking were investigated. Aschan distinguishes between true cracking and a preliminary simplification of complex molecules. True cracking sets in at about 300°-400° C., hydrogen being eliminated. Under high pressure the point of molecular scission is directed to the middle of the molecule but at low pressure the point of rupture is displaced more towards the ends of the molecule and a high gas yield results. Yields and analyses of a large number of oil gases are tabulated and the production of aromatic hydrocarbons and of pure isoprene is discussed. On the basis of a 45% utilisation of masut for cracking it is estimated that 2,584,000 tons of this material would be employed, yielding 1,196,746,000 cub. m. of oil gas, 4,186,080 kilos. of isoprene, 68,463,080 kilos. of benzene, 12,558,240 kilos. of toluene, and 11,498,800 kilos. of oil-gas benzine. The tendency to regard the unsaturated products of cracking as potentially valuable for synthetic chemistry is becoming marked.

ACTION OF REAGENTS ON PETROLEUM.

The action of anhydrous aluminium chloride, which has been proposed on several occasions as a means of cracking petroleum, forms the subject of a paper by A. Pictet and I. Lerczynska[50]; 10% of the reagent dissolves in the higher fractions of petroleum (kerosene to lubricating oils) forming a brown solution which, on being distilled, yields a fraction boiling from 40° to 140° C., almost indistinguishable from straight-run benzine. Kerosene from Galicia yields 50% of cracked benzine, from Baku, 40%, and from Baku lubricating oil, 31%. The latter benzine contained 35% of paraffins and 65% of saturated cyclic hydrocarbons. The residue, on being freed from the reagent, resembles asphalt and is probably formed by the polymerisation of the unsaturated nuclei from which the side-chains have been removed by the action of the aluminium chloride.

[19] Ofversigt af Finska Vetenskaps-Soc. Förhandlingar, Reprint; J., 1919, 401A.
[50] Bull. Soc. Chim., 1916, 19, 326; J., 1917, 1098.

An interesting reaction has been discovered by E. V. Lynn,[51] who has shown that nitrosyl chloride reacts with the lower paraffin hydrocarbons liberating hydrogen chloride and forming a yellow oil which, on being distilled, yielded a mixture of ketones.

J. Tausz [52] proposes to measure the undesirable content of petroleum (e.g., unsaturated hydrocarbons, sulphur derivatives, asphaltic, resinous, and phenolic compounds) by their reaction with alcoholic mercuric acetate and the liberation therefrom of acetic acid.

ORIGIN OF PETROLEUM.

C. F. Mabery [53] has identified nitrogen in the lighter petroleum of the Eastern American field and in the heavier oil of Texas, Oklahoma, Louisiana, Ohio, Kensas, and Baku. These observations, together with analyses made by Mabery and Takano on Japanese oil and the figures quoted by Engler for German, Galician, Roumanian, Sumatran, South American, Egyptian, and Algerian crudes, appear to indicate that the organic theory of the origin of petroleum is well founded.

[51] J. Amer. Chem. Soc., 1919, 41, 368.

[52] Petroleum, 1918, 13, 649; J., 1919, 4A.

[53] J. Amer. Chem. Soc., 1919, 41. 1690; J., 1920, 4A.

COLOURING MATTERS AND DYES.

By FREDERICK M. ROWE, M.Sc., A.I.C.,

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THE outstanding feature of the year 1919 has been the transference of industry from war to peace conditions in this country, which has allowed our rejuvenated colour industry to concentrate its energies on the manufacture of dyes and intermediates, and to relinquish the manufacture of its quota of explosives and poison gases.

In a review of the progress made in this country, it must be frankly admitted that the advent of peace found our colour manufacturers with their programmes for rendering our colour consumers independent of German dyes but half completed. Nevertheless, the progress that has been made is very real, although the occasional outbursts of destructive criticism, emanating in some cases from those who should know better, may have imparted a contrary impression. The astonishing fact is not that progress has been limited in extent, but that our manufacturers have been able to build up the industry to its present proportions under the very trying conditions of the last five years.

The development in this country up to the present time has been mainly in the commoner and cheaper dyes which can be manufactured quickly and in large bulk, and in such classes we have little to fear from competition. With certain exceptions, special and more expensive dyes have been manufactured in comparatively small quantities, the deficiency being met to a certain extent by supplies from Switzerland manufactured largely from British and French raw materials and intermediates, which have replaced similar German materials on which the Swiss were dependent formerly.

The conference on dyestuffs at the Annual Meeting of our Society in London afforded an opportunity for the ventilation of opinions of great value on the position of the industry in this country, the paramount importance of its establishment on a sound and permanent footing,[1] and the policies which might be adopted in order to attain that end.[2] It is clear that although much has been accomplished, much yet remains to be done, particularly with regard to bulk output, for

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[1] H. Levinstein, J., 1919, 246T.
[2] J. Morton, J., 1919, 250T; E. V. Evans, J., 1919, 256T.

the fact that the erection of plant has not kept pace with the progress of technical research has been an important factor in limiting progress in the development of the colour industry. During the war period priority for essential plant could not be obtained, and in addition cases may easily be conceived where the whole material for a particular plant may have been available with the exception of the most essential component part. Further, a great variety of plant is required comprising, as it does, materials such as bronze, copper, glass-enamel ware, lead, nickel, acid-resisting iron, and acid-resisting enamelled steel capable of withstanding sudden changes of temperature and moderately high pressures. In fact, the further development of our industry is largely a question of engineering, and in this connection it is satisfactory to note the prominence recently given to this important subject of chemical engineering.

Much plant and many buildings, therefore, still remain to be erected at high cost, whereas the corresponding German plants were not only erected at a much lower cost but that cost has been already written off. As, moreover, the united capital of the combined German dye and chemical firms approaches £50,000,000, the necessity for continued Government assistance is obvious.

In accordance with the Government scheme for assisting the dye industry, a Trade and Licensing Committee was appointed early in the year, its functions being to determine the colours and intermediate products which shall be licensed for import into the United Kingdom and in what quantities, and to advise the Commissioner of Dyes as to the colours and intermediates the manufacture of which should be specially encouraged and the order of their importance.

The unlicensed importation of intermediates and synthetic dyes was made unlawful by the Prohibition of Import (No. 28) Proclamation of February 25, which is administered by this Committee. Meantime a general licence was issued for the import of dyes of *bonâ-fide* Dominion, American, French, or Swiss origin. In order to make the scheme of control effective this general licence was withdrawn in June, and a Central Importing Agency was established, to which all dyes imported into this country must be consigned.

The assumption has frequently been made that huge stocks of dyes had been accumulated in Germany for the purpose of flooding the market as soon as the war was over, at prices against which our manufacturers would be unable to compete, but as a matter of fact apparently little competition is to be feared from Germany for the time being, as under the Peace Treaty 50% of their stocks as at January 1, 1919, are to be surrendered to the Allies. After satisfying their home demand from the remainder, it would appear that little, if any, will remain for export; moreover, until 1925, 25% of their annual output is to be surrendered to the Allies. It is understood that our share of the first

consignment is now on the way, and the disposal of these dyes, received in part payment of the war indemnity, is receiving attention. These dyes, it is to be hoped, will prove to be those of which we stand most in need, for their arrival—continuing until 1925—would ease the situation and allow our manufacturers a breathing space in which to continue their development and consolidate their position.

With regard to the economic aspect of the dye question, it is to be hoped that efforts towards cheaper production will soon prove fruitful. In this connection it is to be regretted that the reduction in the price of coal, whilst no doubt a great boon to individual householders, is to be effected, apparently, at the expense of industry ; the extension of the reduction to, at any rate, our " key industries " would have proved of very real assistance. On the other hand, as forecasted in last year's Report, there has been a movement towards the levelling up of prices, as the various firms connected with the Interessengemeinschaft have been compelled to increase the price of their products, on account of the stagnation of the industry and the increasing costs of raw materials and labour in Germany.

The amalgamation of the firms of British Dyes, Ltd., and Messrs. Levinstein, Ltd., resulting in the formation of the British Dyestuffs Corporation, Ltd., will allow this country to present a more united front in the future commercial struggle, whilst the acceptance of the position of chairman of this firm by Lord Moulton, has given the greatest satisfaction to all concerned. An increase in the capital of the concern—which now employs about 300 trained chemists and over 6,000 workpeople—to £10,000,000 has been authorised for further developments. The number of products manufactured is steadily increasing and now includes an excellent range of colours of all classes, and whilst the number of colours in this firm's lists starred as available in restricted quantity only is rapidly decreasing, the temporary products of the early days of the war have now been entirely replaced by standard products of recognised purity and value. During the year under review important additions have been made to the number of dyes manufactured, such as : Alizarine Celestol, Coomassie Violet (Formyl Violet S4B), Lissamine Green B (Wool Green S), Gallocyanine BD), Monolite Red R (Lithol Red R), Chrysophenine G, five vat colours, and bases for fur dyeing ; Rhodamine is promised for the near future. The excellent pattern cards issued by this firm with regard to the dyeing of khaki material for civilian purposes were particularly commendable.

Desirable as was the above amalgamation, there is still plenty of scope for individual enterprise, for the numerous firms engaged in colour manufacture in this country can all show a substantial record of progress in quantity, quality, and variety of their products. The number of firms is now too great to allow all to be mentioned here, but

some instances may be quoted. Messrs. L. B. Holliday & Co., Ltd., only commenced the production of dyes and drugs early in 1918; within six months 20 individual products were being manufactured with a total output of 50 tons per month, while at present these figures have been trebled and they will no doubt continue to increase as further extensions which are in progress are completed.

The Solway Dyes Co. are supplying the home market with continuously increasing quantities of fast dyes of a quality fully equal to their pre-war German equivalents : small quantities have also been exported, and it is hoped to supply the needs of foreign buyers as the output increases. Kymric Green and Solway Purple, which replace Alizarine Cyanine Green and Alizarine Irisole respectively, are being manufactured. The business of this firm is now being prosecuted on a larger scale under the name of Scottish Dyes, Ltd., and a site of 80 acres has been acquired at Grangemouth for the erection of a new colour works.

Messrs. Brotherton & Co., Ltd., have increased their range. of metachrome colours, and are manufacturing hydrosulphite compounds with considerable success. The British Alizarine Co. are contemplating considerable extensions in their business, and the erection of a large new works at Trafford Park, Manchester, is in progress.

Messrs. H. N. Morris & Co., Ltd., have practically completed a large installation for the chlorination of toluene and the manufacture of benzyl chloride, benzaldehyde, and benzoic acid.

Messrs. Hickson & Partners, Ltd., whose works is erected on a fine site near Castleford, make a speciality of rosaniline base, and put magenta on the market under its original name of Roseine, but their main business at present consists in the manufacture of a number of intermediates.

The number of intermediates manufactured by the large gas companies has increased during the period under review.

At the present moment the list of dyes which need never be purchased from Germany again is large and ever-increasing, and granted the good-will of the consumer, the expansion of our colour industry to the point when it will satisfy, not only our own requirements, but those of our Empire and other markets is mainly a question of time. It is unreasonable to expect, as some critics appear to do, our rejuvenated industry to be able to supply the whole range of pre-war German dyes at competitive prices after only five years, especially as the nation was engaged in fighting and winning the greatest war in history during that period.

Progress in America has followed somewhat similar lines to our own, the principal development being in the azo, sulphide, and induline classes, but although the output of synthetic indigo is increasing, there is still much scope for development in other classes. Carbazole is

now obtainable, but technical difficulties must be overcome before anthracene will be available in adequate quantity at a reasonable price, as tar from American coal contains only 0·3% of anthracene, and its recovery is a matter of difficulty.

The Chemical Foundation, whose aim is to secure the licensing of certain dye imports and the exclusion of dyes reasonably obtainable in America, on lines similar to those of our own Licensing Committee, was organised in New York in the spring, and 150 of the leading American manufacturers enrolled in it.

According to the latest reports, about 60 dyes, including direct, basic, acid, mordant, and sulphide colours, together with some indigo, are being manufactured in Japan on the large scale, but the home production has been unable to satisfy the demand; even in the simpler dyes it will be a number of years before she can satisfy her own requirements, whilst it is probable that the importation of vat dyes and the more complex direct cotton colours will be always necessary.

The companies established in France for the manufacture of dyes and chemicals most probably will require a number of years before they will be in a position to cope entirely with their home demand, whilst the possibility of Italy satisfying her own requirements is even more remote.

It is clear, therefore, that many markets will be open to British colour manufacturers for the disposal of surplus stocks of those dyes which may be manufactured in considerable bulk, and it is to be hoped that they will be able to seize this opportunity of laying the foundation of a permanent export trade.

INTERMEDIATES.

Sulphonation.

The sulphonation process has continued to attract much attention, particularly with regard to the development of systems for the continuous sulphonation of hydrocarbons in the state of vapour, and the preparation of benzenemonosulphonic acid by the continuous process, together with the plant employed, has been described in detail.[3] In the preparation of monosulphonic acids of the benzene series, the vapour of the hydrocarbon and sulphuric acid react, whilst the excess of hydrocarbon and water are removed as vapour,[4] or the vapour is passed through a steam superheater at a temperature of 160°–200° C. on the way to the heated sulphuric acid.[5]

Continuous sulphonation on the counter-current system is effected

[3] A. Guyot, *Chim. et Ind.*, 1919, 2, 879; J., 1919, 811A.

[4] J. A. Ambler and H. D. Gibbs, U.S. Pats. 1300227 and 1300228; J., 1919, 405A.

[5] Comp. des Produits Chimique d'Alais et de la Camargue, Eng. Pat. 126039; J., 1919, 405A.

in a system of tanks arranged in steps, in which the hydrocarbon—always theoretically in excess of the acid—enters at the bottom of the lowest tank, and passes upward through the acid, so that hydrocarbon rich in sulphonic acid is removed from the top tank, whilst weak acid, free from sulphonic acid, is drawn off from the bottom tank.[6] Alternatively, a continuous stream of fuming sulphuric acid is led through a heater into the top of a column, whilst benzene vapour is introduced at the bottom and is sulphonated as it rises, whereby the hot sulphonic acid flows out at the bottom and is used for pre-heating a further supply of benzene.[7] This process, which is particularly adapted for the sulphonation of benzene containing petroleum (as the latter is removed unchanged in the form of vapour from the top of the column and condensed), with suitable modifications may be applied to the sulphonation of other hydrocarbons;[8] toluenesulphonic acids, for example, are produced by bringing toluene vapour in contact with a descending current of sulphuric acid,[9] whilst a continuous process for the sulphonation of cymene also has been patented.[10]

Economy in the quantity of sulphuric acid results from heating the sulphonation mixture, obtained in the monosulphonation of benzene, to $130°$–$180°$ C. in a vacuum, so that the ratio of water to free sulphuric acid is sufficiently reduced to render the excess acid available for the sulphonation of a further quantity of benzene,[11] or the excess sulphuric acid may be recovered from the sulphonation mixture and the sulphonic acid isolated, by distillation in a high vacuum at a temperature below that at which the sulphonic acid decomposes.[12]

Toluene, when sulphonated in a partial vacuum, forms mainly the parasulphonic acid at $150°$ C., and disulphonic acids at $240°$–$250°$ C., whilst naphthalene forms the β-monosulphonic acid at temperatures below its normal boiling-point, and the 2 7-disulphonic acid at $220°$-$230°$ C.[13]

The readily soluble sulphates of certain di- and tri-valent metals, particularly magnesium and aluminium, are used with advantage for the isolation of sulphonic acids from sulphonation mixtures in the form of salts, which, although soluble in water to the extent of 5–25%, are more sparingly soluble in dilute sulphuric acid of 30–50% strength.[14]

[6] H. Bull, Eng. Pat. 118727; J., 1919, 619A.

[7] E. Barbet et Fils et Cie., Eng. Pat. 127614; J., 1910, 529A.

[8] E. Barbet et Fils et Cie., Eng. Pat. 132298; J., 1919, 813A.

[9] J. A. Ambler and H. D. Gibbs, U.S. Pat. 1292950; J., 1919, 280A.

[10] J. A. Ambler, H. A. Lubs, and H. D. Gibbs, U.S. Pat. 1316823; J., 1919, 813A.

[11] E. S. Beach, U.S. Pat. 1301360; J., 1919. 495A.

[12] The Barrett Co., U.S. Pat. 1301785; J., 1919, 495A.

[13] H. D. Gibbs, J. A. Ambler, and The Selden Co., Eng. Pat. 131970; J., 1919, 756A.

[14] A. Lapworth and H. N. Morris, Eng. Pat. 14402/1915; J., 1919, 280A.

Alkali Fusions.

Investigation has demonstrated that a loss in yield occurs when the alkaline fusion of sodium benzenesulphonate is carried out in open pans,[15] for oxygen is absorbed and free hydrogen evolved when the fusion with caustic soda is effected in presence of air, whereas no hydrogen is evolved when air is excluded. A double oxidation appears to take place, first by atmospheric oxygen and then by water, with hydrogen formation. The maximum yield of phenol is 90% when the fusion is carried out in presence of air, whilst up to 98% of the theoretical yield is obtained by effecting the fusion in an atmosphere of nitrogen.

The objectionable odour which is noticed in the case of some samples of synthetic phenol has been attributed to the presence of thiophen in the benzene employed in the process, but this odour is really due to the formation of a small quantity of thiophenol from particles of sodium benzenesulphonate which escape contact with the alkali during the fusion and undergo deoxidation at the surface of the iron vessel.[16] The thiophenol is removed by treatment with an alcoholic solution of mercuric chloride.

An interesting development has been the application of electrolysis to the products of the alkaline fusion of aromatic sulphonic acids.[17] The alkali sulphite, formed as a by-product of the fusion, is extracted with a minimum quantity of water and electrolysed, whereby caustic alkali is formed, and the sulphur dioxide which is liberated is used for sulphuric acid manufacture or for the decomposition of the alkali hydroxy-compound, with re-formation of alkali sulphite, which is electrolysed in its turn. Alternatively, the whole melt is dissolved in water and electrolysed, phenol, for example, being liberated at the anode and caustic soda at the cathode.

The liquid fusion process, to which reference was made in a former report,[18] has been extended to the production of naphthols and allied products, in which case a concentrated aqueous solution of a salt of a naphthalenesulphonic acid, at a temperature of about $100°$ C., is run gradually into a covered vessel containing fused caustic alkali at about $300°$ C.[19]

Nitro-compounds.

The production of polynitrophenols has been the subject of numerous investigations during the year under review, and the construction of

[15] M. C. Boswell and J. V. Dickson, J. Amer. Chem. Soc., 1918, 40, 1786; J., 1919, 69A.

[16] G. Cappelli, Gazz. Chim. Ital., 1918, 48, 107.

[17] South Metropolitan Gas Co., and E. V. Evans, Eng. Pat. 129002; J., 1919, 676A.

[18] Ann. Repts., 1918, 91.

[19] R. N. Wallach, U.S. Pat. 1291300; J., 1919, 248A.

plant for the continuous nitration of organic liquids has received further attention.[20]

A yield of 71% of 2.4-dinitrophenol is obtained by the direct nitration of phenol.[21] In the process for the production of 2.4-dinitrophenol by the nitration of benzene in presence of mercuric nitrate, the reaction is greatly facilitated by passing a current of carbon dioxide, air or oxygen, or a mixture of air and oxygen with or without carbon dioxide, into the nitration mixture,[22] whilst the formation of by-products during the process is avoided by removing the product as it is formed, by circulating the reaction mixture through the nitrator, a cooling coil, and a filter, the filtrate being then returned to the nitrator.[23]

Polynitrophenols are conveniently prepared by passing a current of nitrous gases through an aqueous solution or suspension of the ortho- or para-sulphonic acids of aniline or its homologues, provided that either the ortho- or para-position with respect to the amino-group is unoccupied. A yield of 90% of picric acid, for example, is obtained from aniline-o- or p-sulphonic acid by this method.[24]

The production of compounds of the type of picric acid from the corresponding phenols should undoubtedly be carried out in stages, as in that case no nitrous fumes are evolved, and the quantities of sulphuric and nitric acids required are only slightly in excess of the theoretical. Phenol, for instance, is first converted into its p-sulphonic ac.¹: the sulphonation mixture is diluted with water and run into a cold solution of sodium nitrate, by which means sodium 2-nitrophenol-4-sulphonate is formed. Addition of nitric acid produces a mixture of 2.4-dinitrophenol and sodium 2.6-dinitrophenol-4-sulphonate, the former is removed by filtration, and pure picric acid, in good yield, is obtained from the latter by adding nitric acid to the filtrate and bringing the mixture to the boil.[25] In the application of this method to the nitration of commercial cresol, the o- and p-isomers are converted into their insoluble 3.5-dinitro-derivatives, which are removed by filtration, whilst the filtrate contains sodium 2.4-dinitro-m-cresol-6-sulphonate, from which trinitro-m-cresol is formed by boiling with nitric acid.

A novel method of nitration by which nitrobenzene, m-dinitrobenzene, and o- and p-nitroanisole may be prepared consists in passing

²⁰ The Clayton Aniline Co., A. Schedler, and V. Vuilleumier, Eng. Pat. 126353.
²¹ M. Marqueyrol and P. Loriette, *Bull. Soc. Chim*, 1919, **25**, 375; *J.*, 1919, 675ʌ.
²² D. B. Macdonald and J. Calvert, Eng. Pats. 126062 and 126084; *J.*, 1919, 106ʌ.
²³ T. J. Brewster, Eng. Pat. 131403; *J.*, 1919, 812ʌ.
²⁴ R. L. Datta and P. S. Varma, Eng. Pat. 126321; *J.*, 1919, 495ʌ.
²⁵ M. Marqueyrol and P. Loriette, *Bull. Soc. Chim*, 1919, **25**, 370; *J.*, 1919, 697ʌ.

oxygen, air, or ozonised air, preferably under pressure, into a mixture of the substance to be nitrated, liquid nitrogen peroxide, and traces of water at $0°-20°$ C.[26]

The nitration of hydrogenised derivatives of naphthalene is a matter of difficulty owing to the oxidation and resinification of the products. Recent experiments carried out by the writer have met with success and have been confirmed by the production of α- and β-mononitro-tetrahydronaphthalene and 1.3-dinitrotetrahydronaphthalene.[27]

A detailed study of the action of nitrous and nitric acids on diphenyl-amine has been made,[28] and a number of nitro-derivatives of phenyl-2-naphthylamine have been prepared and examined.[29]

Aromatic Amines.

Further investigations have been carried out on the catalytic reduction of nitro-compounds. Nitrophenols are not reduced readily by hydrogen in presence of nickel at $160°-190°$ C., but a more efficient reduction, which results in practically quantitative yields of pure, white aminophenols, is obtained by passing a mixture of o- or p-nitrophenol vapours and hydrogen over copper deposited on pumice at $265°$ C.[30] Pure phenylenediamines are prepared in a similar manner from nitroanilines and m-dinitrobenzene, but naturally the process is slower, on account of the lower volatility of these compounds.

During the catalytic reduction of nitrobenzene to aniline only traces of phenylhydroxylamine can be detected, but it is reasonable to conclude that the reduction passes through this intermediate stage, because anthranil and methylanthranil are obtained from o-nitro-benzaldehyde and o-nitroacetophenone respectively, under similar conditions,[31] and in these cases a hydroxylamine derivative must be formed as an intermediate compound, e.g.,

$$C_6H_4{\diagup}^{NH_2}_{\diagdown COH} \longrightarrow C_6H_4{\diagup}^{NH.OH}_{\diagdown COH} \longrightarrow C_6H_4{\diagup}^{\underset{C}{\overset{N}{\diagdown}}}_{\diagdown\underset{H}{}}{\diagdown} O$$
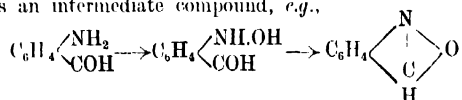
A modification of Bamberger's method for the preparation of hydrogenised naphthalene derivatives, which is more convenient in practice, has been described, and it is claimed that ar-tetrahydro-α-naphthylamine is formed when an alcoholic solution of α-naphthylamine is added to a mixture of an indifferent solvent, such as solvent naphtha, and sodium

[26] Gros et Bouchardy, and L. J. J. Perruche, Eng. Pat. 131982 ; J., 1919, 812A.
[27] Tetralin G.m.b.H., Ger. Pat. 299014 ; J., 1920, 174A.
[28] H. and P. Ryan, Proc. Roy. Irish Acad.. 1918, 34, B, 194, 212 ; J., 1919, 742A.
[29] H. Ryan and J J. Drumm, Proc. Roy. Irish Acad., 1918, 34, B, 165 ; J., 1919, 741A.
[30] O. W. Brown and L. L. Carrick, J. Amer. Chem. Soc., 1919, 41, 436.
[31] F. F. Nord, Ber., 1919, 52, 1705 ; J., 1920, 56A.

at a temperature above 130° C., whereas the previously unknown dihydro-α-naphthylamine is obtained by the use of an indifferent solvent of lower boiling-point, such as toluene.[32] The suggestion has been advanced previously that the important factor in the preparation of ar-tetrahydro-α-naphthylamine is the nature of the particular alcohol employed,[33] and it is found that even in this modified method the tetrahydro-compound is formed, under ordinary conditions, only when amyl alcohol is used, whilst with other alcohols, dihydro-α-naphthylamine is formed, irrespective of the boiling-point of the indifferent solvent.[34]

Good yields of pure amino-bases, capable of diazotisation and suitable for producing red, claret, khaki, or yellow azo-colours on the fibre, fast to washing, alkalis, and acids, are obtained by treating aromatic amines with a slight excess of formaldehyde in presence of dilute mineral acids and boiling the mixture.[35]

Much attention has been devoted to the production and purification of N-alkylarylamines during the year. The preparation of monomethylaniline by the following methods has received detailed study : [36]

(1) Reduction of methylene-aniline with zinc dust and caustic soda.

(2) Heating aniline hydrochloride with methyl alcohol in an autoclave at 180°-200° C.

(3) Demethylating dimethylaniline by heating with aniline hydrochloride at 200° C.

The maximum yield of monomethylaniline is about 55% in each case. Aniline is readily separated from monomethylaniline by conversion into its zincichloride.

The fact that primary and secondary, but not tertiary amines, react with ethyl chloroformate in the cold, in presence of aqueous sodium carbonate, to form the corresponding urethanes, is utilised for the separation of the mixed bases.[37] The unchanged tertiary amine is extracted from the mixture with dilute mineral acid, and the primary and secondary amines are regenerated from the urethanes by hydrolysis.

Mixtures of secondary and tertiary amines, which contain an excess of the latter, are treated with phosgene whereby the former is converted into an urea chloride. The unaltered tertiary amine is extracted with dilute hydrochloric acid, and the secondary amine is regenerated from the insoluble urea chloride by boiling with water or dilute hydrochloric

[32] F. Bayer & Co., Ger. Pats. 305347 and 306724 ; J., 1918, 487A ; 1919, 158A.

[33] A. G. Green and F. M. Rowe, Chem. Soc. Trans., 1918, 113, 955.

[34] F. M. Rowe, J. Soc. Dyers and Col., 1919, 35, 128 ; J., 1919, 406A

[35] A. M. Nastukoff and P. M. Croneberg, Ger. Pat. 308839 ; J., 1919, 37A.

[36] P. F. Frankland, F. Challenger, and N. A. Nicholls, Chem. Soc. Trans., 1919, 115, 198 ; J., 1919, 338A.

[37] W. Rintoul, J. Thomas, and Nobel's Explosives Co., Eng. Pat. 127740 ; J., 1919, 600A.

acid.[38] Should the mixture contain an excess of secondary amine, tertiary amine is added in quantity sufficient to produce an excess, or the above operation is repeated.

An ingenious method for the preparation of the N-monoalkyl derivatives of monoamines, such as *p*-aminophenol, *p*-toluidine, or their derivatives, which do not, either as amines or N-alkylamines, react with benzaldehyde in presence of acids to form amino derivatives of triarylmethanes, consists in treating the benzylidene derivative of the amine with alkyl sulphates or alkyl esters of benzenesulphonic acid in absence of alkali, followed by hydrolysis and separation of the N-monoalkylarylamine.[39]

N-methyl-*p*-aminophenol is prepared by heating quinol and methylamine together at 150° C. for five hours.[40]

Diphenylamine is obtained by heating aniline in presence of water and a catalyst comprising a substance containing bromine.[41]

An addition has been made to the number of products available for dye manufacture by the discovery that β-naphthylmethylamine, $C_{10}H_7NH.CH_3$ is formed in good yield and in a high state of purity by the interaction of β-naphthol and aqueous methylamine at 200°-220° C.[42] The simple azo derivatives of this compound have been studied and their dyeing properties recorded.

Halogenation.

Interesting developments in the halogenation of hydrocarbons under the influence of actinic light are recorded ; thus, the halogen derivatives of hydrocarbons are prepared by exposing a gaseous mixture of the halogen and the hydrocarbon to actinic light of gradually increasing intensity in a suitable transparent vessel.[43] In the case of toluene, chlorination is effected by subjecting a mixture of toluene vapour and chlorine to the action of ultra-violet light, and benzal chloride or benzotrichloride is formed according to the proportion of chlorine present.[44] If a " low pressure " mercury vapour lamp is used at a temperature of 150° C., benzyl and benzal chlorides are formed almost exclusively, but the main product is benzotrichloride when a " high pressure " lamp is used.[45]

Chlorination of purpurine and other similarly constituted hydroxy-

[48] W. Rintoul, J. Thomas, and Nobel's Explosives Co., Eng. Pat. 128372 ; *J.*, 1919, 657A.

[49] A. Lapworth, and Levinstein, Ltd., Eng. Pat. 132555 ; *J.*, 1919, 847A.

[40] R. N. Harger, U.S. Pat. 1297685 ; *J.*, 1919, 406A.

[41] E. I. du Pont de Nemours & Co., U.S. Pat. 1314538 ; *J.*, 1919, 813A.

[42] G. T. Morgan and F. P. Evans, *Chem. Soc. Trans.*, 1919, **115**, 1140 ; *J.*, 1919, 893A.

[43] W. O. Snelling, U.S. Pat. 1285823 ; *J.*, 1919, 158A.

[44] H. D. Gibbs and G. A. Geiger, U.S. Pat. 1246739 ; *J.*, 1919, 52A.

[45] The Selden Co., and H. D. Gibbs, Eng. Pat. 123341 ; *J.*, 1919, 268A.

anthraquinones, such as Alizarine Cyanine R, Alizarine Green G, Anthracene Blue WR, and their sulphonated derivatives, in hot nitro-benzene solution, is effected by means of sulphuryl chloride in presence or absence of iodine, and according to the conditions, one or more of the hydroxyl groups is replaced by chlorine.[46] Alizarine and its sub-stitution products such as flavopurpurine, anthrapurpurine, Alizarine Bordeaux, α- and β-nitroalizarine, rufligallol, Alizarine Garnet, and sulphonated alizarine are chlorinated in a similar manner, forming mono- or poly-chloro derivatives.[47] These chlorinated compounds are mordant dyes for wool.

Juglone (5-hydroxy-1.4-naphthaquinone) has been the subject of an interesting investigation which led to the preparation of a new type of colouring matter.[48] Juglone dichloride or dibromide, formed by the action of chlorine or bromine on a cold acetic acid solution of juglone, is converted into 2-chloro- (or bromo-) juglone by treatment with alcohol, with elimination of a molecule of hydrogen halide. Halo-genation proceeds further at higher temperatures, chlorine producing 2.3-dichlorojuglone and bromine 2.3.8-tribromojuglone. On treat-ment with alcoholic hydrogen chloride the latter is converted into 2.3-dibromo-8-chlorojuglone, whilst alcoholic caustic soda converts it into 2.3-dibromo-8-hydroxyjuglone (2.3-dibromo-5.8-dihydroxy-1.4-naphthaquinone). 2.3.8-Tribromojuglone is a brilliant red compound which is converted into its sodium salt, an indigo-blue substance, by shaking an ethereal solution with aqueous sodium carbonate. This salt gives wool and silk in fast shades which may be modified by the use of mordants. Juglone should possess dyeing properties, but attempts to prepare its sodium salt proved unsuccessful owing to oxidation.

Oxidation.

Benzaldehyde is produced in a practically pure condition by boil-ing benzyl bromide with a solution of sodium or calcium nitrate,[49] but when benzyl chloride and lead nitrate are used, benzoic acid also is formed.

Aromatic aldehydes, free from carboxylic acid, are obtained by boiling chloromethylene derivatives with an aqueous solution of an alkali bichromate, preferably with the addition of an alkali hydroxide or carbonate, according to the general equation:

$$3R \cdot CH_2Cl + Na_2Cr_2O_7 + NaOH \quad 3R \cdot CHO + 3NaCl + CrO_3 + 2H_2O.$$
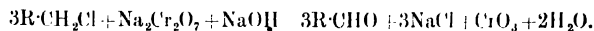
[46] L. B. Holliday & Co., and H. D. Law, Eng. Pat. 126527 ; J., 1919, 457A.

[47] L. B. Holliday & Co., and H. D. Law, Eng. Pat. 126528 ; J., 1919, 457A.

[48] A. S. Wheeler and J. W. Scott, J. Amer. Chem. Soc., 1919, 41, 833 ; J., 1919, 712A.

[49] The Dow Chemical Co., U.S. Pat. 1272522 ; J., 1919, 268A.

An almost theoretical yield of *p*-toluic aldehyde, for example, is obtained by this method.[50]

Benzaldehyde, moreover, may be produced direct from toluene by digesting with manganese dioxide in presence of an acid and a catalyst such as ferric, copper, or cerium sulphate, followed by fractionation to separate the aldehyde from unchanged toluene.[51]

The action of oxidising agents on alizarine in presence of alkalis has been the subject of an interesting investigation. The oxidation of alizarine with an aqueous solution of potassium ferricyanide and potassium hydroxide at the ordinary temperature results in the formation of 2-hydroxy-1·4-naphthaquinone-3-vinylglyoxylic acid,[52]
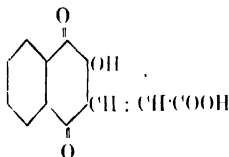
On the other hand, when the oxidation is effected with potassium hypochlorite under similar conditions, 3.4.3′.4′-tetrahydroxy-2.2′-dianthraquinonyl
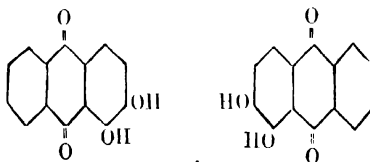
is formed.[53] It has no affinity for unmordanted fibres, and is a much poorer mordant dye than alizarine.

Condensations.

Phthaleins are mainly or exclusively formed by the condensation of 1·6-dihydroxynaphthalene and phthalic anhydride, with or without the presence of the usual condensing agents such as zinc chloride, but in presence of boric acid, 1.6-dihydroxynaphthoyl-*o*-benzoic acid, $(HO)_2C_{10}H_5 \cdot CO \cdot C_6H_4 \cdot COOH$, the intermediate product in the formation of the phthalein, is mainly formed.[54] This acid and its salts, which possess a very sweet taste, may be used as sugar substitutes, or as intermediate products for dyes, and when printed on cotton or wool

[50] G. Blanc. Eng. Pat. 115244 ; *J.*, 1919, 440A.
[51] The Import and By-Products Co., U.S. Pat. 1302273 ; *J.*, 1919, 877A.
[52] R. Scholl and A. Zinke. *Ber.*, 1918, 51, 1419; *J.*, 1918, 763A.
[53] R. Scholl, *Ber.*, 1919, 52, 1829 ; *J.*, 1920, 57A.
[54] Soc Chem. Ind. Basle, Ger. Pat. 311213.

by the methods used for chrome colours produce bright greenish-yellow shades, fast to light and washing, whilst the corresponding 1,5-acid yields orange shades which are much less fast to light.

Dyes analogous to the phthaleins are formed by the condensation of quinolinic acid with resorcinol, catechol, phloroglucinol, *m*-phenylenediamine, *m*-dimethylaminophenol, or 2.1-diaminophenol.[55] A comparison of these dyes with the corresponding phthaleins shows that the presence of the nitrogen atom in the ring lightens the colour and diminishes the fluorescence. Further, the greater the power of the auxochromic group to deepen the colour of the dye the greater is its effect on the fluorescence; thus *m*-dimethylaminophenol-quinolinein,
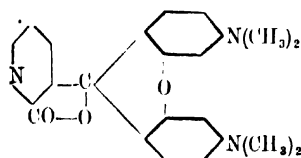
has the deepest colour (reddish-violet) in the series and is the most strongly fluorescent.

DI- AND TRI-PHENYLMETHANE DYES.

The treatment of commercial xylidine, which is a mixture of a number of isomers, with an excess of benzaldehyde in presence of acids results in the condensation of the para-compound with formation of 4.4'-diamino-2 2'.5.5'-tetramethyltriphenylmethane, $C_6H_5 \cdot CH[NH_2 \cdot C_6H_2 (CH_3)_2]_2$, in a yield of about 15% of the weight of xylidine used.[56]

The product of the condensation of *o*-phthalaldehyde with dimethylaniline varies with the reaction conditions. The leuco base of *o*-phthalaldehyde green (I) is the chief product obtained by heating *o*-phthalaldehyde, more than 6 molecular proportions of dimethylaniline, and zinc chloride for 2 hours at 120° 130° C., but *o*-aldehydoleucomalachite green (II) is the main product when *o*-phthalaldehyde, 2 molecular proportions of dimethylaniline, and zinc chloride are heated together for 1 hour at 100°–110° C.[57] Both leuco bases are converted into olive green dyes by oxidation.

$$C_6H_4 \begin{cases} CH[C_6H_4 \cdot N(CH_3)_2]_2 \\ CH[C_6H_4 \cdot N(CH_3)_2]_2 \end{cases} \qquad C_6H_4 \begin{cases} CH[C_6H_4 \cdot N(CH_3)_2]_2 \\ CHO \end{cases}$$

I.   II.
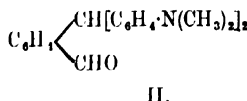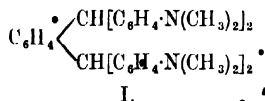
[55] P. C. Ghosh, *Chem. Soc. Trans.*, 1919, **115**, 1102; *J.*, 1919, 813A.
[56] Meister, Lucius and Brüning, Ger. Pat. 308785; *J.*, 1919, 37A.
[57] E. Weitz, *Annalen*, 1919, **418**, 1.

In spite of the fact that the reducing action of sodium hydrosulphite or dyes has been the subject of much attention in the past, a reaction with this reagent, peculiar to dyes of the di- and triphenylmethane classes, has escaped observation. The leuco base of Crystal Violet, for example, is obtained, as is well known, by the addition of hydrosulphite to an alcoholic solution of the dye, yet there is no separation of the leuco base when hydrosulphite is added to an aqueous alkaline solution of the dye, and the colourless solution obtained has the properties of a vat, for material steeped in it, and exposed to air, is oxidised instantly to the dyed shade.[58] Basic and acid triphenylmethane dyes, Aurin, the simpler phthaleins, and the fluoresceins behave in the same manner with alkaline hydrosulphite. In the case of Crystal Violet (I), the reduction product may be isolated in a pure crystalline condition [59] and appears to be a derivative of a sulphinic acid (III) or sulphoxylic ester (IV):

$$[(CH_3)_2N \cdot C_6H_4]_2C : C_6H_4 : N(CH_3)_2Cl.$$

I.

$$[(CH_3)_2N \cdot C_6H_4]_2C(SO_2Na) \cdot C_6H_4 \cdot N(SO_2Na)(CH_3)_2Cl.$$

II. (Intermediate stage.)

$$[(CH_3)_2N \cdot C_6H_4]_2C(SO_2Na) \cdot C_6H_4 \cdot N(CH_3)_2 + NaCl + SO_2.$$

III.

$$[(CH_3)_2N \cdot C_6H_4]_2C(O.SO \cdot Na) \cdot C_6H_4 \cdot N(CH_3)_2 + NaCl + SO_2.$$
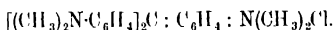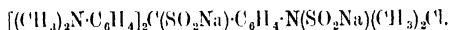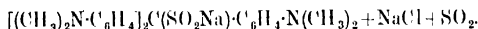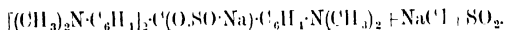
IV

The course of the autoxidation of compounds of the type of III and IV is not clear.

The isomeric compounds, $C_{15}H_{14}O$, named pyrocresols,[60] isolated from the residue of the distillation of crude coal-tar phenol, and identical with the compounds prepared by the decomposition of aluminium o-, m-, and p-tolyloxides,[61] are dimethylxanthens. The high-boiling liquids obtained at the end of the distillation of aluminium phenoxide are derived from xanthen and phenol, thus:

$$C_{13}H_{10}O + C_6H_5 \cdot OH = C_{19}H_{14}O + H_2O.$$
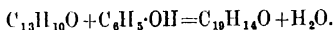
A brown colouring matter, Xanthen Brown, is obtained from this phenylated xanthen by successive nitration and reduction, and is an inner ester of Magenta with the constitution:[62]

[58] H. Wieland. Ger. Pat. 308298 ; J_c, 1919, 10A.
[59] H. Wieland, Ber., 1919, 52, 880 ; J., 1919, 456A.
[60] H. Schwarz, Ber., 1882, 15, 2201 ; J.; 1882, 442.
[61] J. H. Gladstone and A. Tribe, Chem. Soc. Trans., 1886, 49, 25.
[62] F. Ruszig, Z. angew. Chem., 1919, 32, 37 ; J., 1919, 217A.

$$NH_2 \cdot C_6H_4 \cdot C \begin{cases} C_6H_3 \cdot NH_2 \\ {>}O \\ -C_6H_3 \\ NH_2Cl \end{cases} , \quad \text{or} \quad \begin{matrix} C_6H_4 \\ | \\ Cl \cdot NH_2 \end{matrix}{>}C \begin{cases} C_6H_3 \cdot NH_2 \\ {>}O \\ C_6H_3 \cdot NH_2 \end{cases}$$
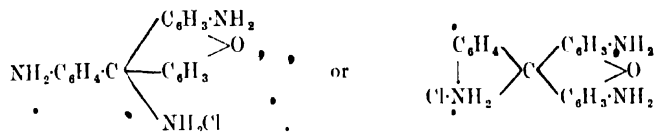
A simple photo-chemical reaction has been developed from the well-known behaviour of triphenylmethane dyes with potassium cyanide. The coloured dye-cyanide (II), primarily formed by the addition of potassium cyanide to a solution of a salt of a triphenylmethane dye, such as p-Rosaniline (I), passes over into the colourless triarylaceto-nitrile (III), thus:
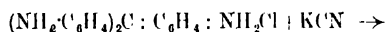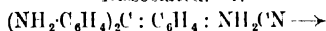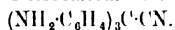
$$(NH_2 \cdot C_6H_4)_2C : C_6H_4 : NH_2Cl + KCN \longrightarrow$$
Dissociated. I.
$$(NH_2 \cdot C_6H_4)_2C : C_6H_4 : NH_2CN \longrightarrow$$
Dissociated. II.
$$(NH_2 \cdot C_6H_4)_3C \cdot CN.$$
Undissociated. III.

The reaction is reversible, for the colour of the solution is restored on exposure to ultra-violet light, and slowly disappears again when placed in a dark room at the ordinary temperature, or more rapidly when warm.[63]

The maximum optical effect or typical colour is reached in the case of the quinonoid salts of nitro- and amino-triphenylmethanes when two salt-forming groups are present in the molecule, and furthermore the fuchsins closely resemble the reddish-violet salts of the aminoazo-benzenes. These three classes of compounds contain a quinonoid salt complex as chromophore and another group which forms a powerful auxochrome in conjugation with the quinonoid group, thus[64]:

$$\begin{matrix} Ar \cdot C & C_6H_4 & NO_2 & Ar \cdot C & C_6H_4 - NR_2 & N & C_6H_4 - NR_2 \\ | & | & & | & | & | & | \\ Ar \cdot NO_2 \ldots \ldots M & & Ar \cdot NR_2 \ldots \ldots X & & NAr \cdot R \ldots \ldots X \end{matrix}$$
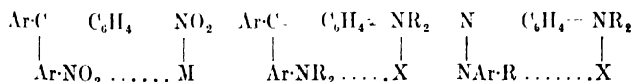
Nitrotriphenylmethanes.   Aminotriphenylmethanes.   Aminoazo-salts.

PYRONE COLOURS.

The mother substance of Quercitron Bark, Old Fustic, and other yellow natural colouring matters is flavone (benz-2-phenyl-γ-pyrone):

$$\begin{matrix} & O \\ & \diagup \\ & C \cdot C_6H_5 \\ & | \\ & CH \\ & \diagdown \\ & CO \diagup \end{matrix}$$
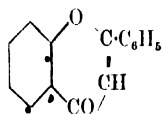
[63] J. Lifschitz, Ber., 1919, 52, 1919.
[64] A. Hantzsch and F. Hein, Ber., 1919, 52, 193, 509; J., 1919, 495A.

derivatives of pyrazolone, or rather of oxypyrazole, the tautomeric form of pyrazolone The monoazo colours are mostly yellow to orange in shade; whilst red, blue, and violet dyes are derived from tetrazotised diamines of the benzidine type coupled with either two molecules of a pyrazolone or one molecule of a pyrazolone and one molecule of a phenol, salicylic acid, etc , or more generally, in the latter case, an aminopoly-azo compound is diazotised and developed on the fibre with a pyrazo-lone.

Mono azo dyes of the pyrazolone series of the general type :

$$N \quad C\text{-}CH_{3}$$
$$| \quad C\text{-}N\,.\,N\,R'$$
$$NR''\text{-}C\text{-}OH$$
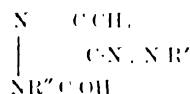
are obtained by coupling the diazonium compound of an amine, which does not contain a hydroxyl or carboxyl group in the ortho position with respect to the amino group, with a derivative of 1-phenyl-3-methyl-5 pyrazolone containing a hydroxyl or carboxyl group in the phenyl residue.[75]

Acid disazo dyes, capable of producing fast green shades when after-chromed, are produced by coupling o hydroxydiazonaphthalenesul-phonic acids with a concentrated alkaline solution of m-aminophenol or one of its derivatives in which the para position with respect to the amino group is free , the aminoazo compound formed is diazotised and coupled with a compound containing the grouping --C(OH) : CH-, such as an arylpyrazolone, an aceto-acetic acid arylide, etc.[76]

The property of forming lakes with metallic mordants is not confined to azo dyes which contain two hydroxyl groups contiguous to the azo group, for a pair of hydroxyl and amino groups in this position brings about the same effect , it is assumed that a new cyclic complex is produced in which the metal, the azo group, and the two adjacent auxo-chromic groups take part by virtue of principal valency and also by residual valency [77] The lake of Metachrome Brown B for example, is thus :

$$
\begin{array}{c}
O\quad M..\quad....NH_2 \\
O_2N \diagdown \langle \quad \rangle \text{-}N\,N\text{-}\langle \quad \rangle NH_2 \\
O_2N \diagup \qquad\qquad CH_3
\end{array}
$$
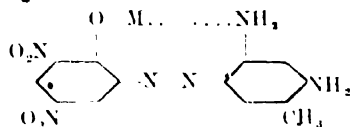
Mordant monoazo dyes of the same type are obtained by coupling p-mononitro-o-hydroxydiazo-aryl compounds which do not contain

[75] Soc. Chem Ind. Basle, U.S Pat. 1286451 ; J , 1919, 130A.
[76] Soc. Chem. Ind. Basle, Eng. Pat. 128726 ; J., 1919, 677A.
[77] G. T. Morgan, J., 1919, 255т.

sulphonic groups with sulphonic acids of β-naphthylamine.[78] e.g.,
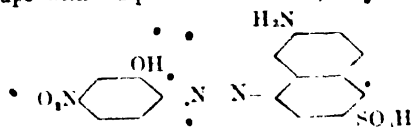
These dyes form pure green chromium lakes, fast to light and insensitive to copper. Mordant monoazo dyes are produced by diazotising a compound of the general formula: $(HO_1(1)(NH_2(2)-R\,SO_2\,NH-X$, where R is an aryl residue and X a hydrogen atom or an aryl residue which may contain one or more substituents, and coupling with a suitable component.[79] Disazo dyes in the same series are prepared by tetrazotising a compound of the same general formula, but in which R is an aryl residue and X an aryl residue containing an amino group, or where X is the residue $-SO_2\,R'(OH_a1)(NH_2(2)$ and R' an aryl residue, identical or not with R, and coupling with two molecular proportions of a suitable component or with one molecular proportion of each of two components. Dyes of this type may be dyed on wool and after treated with copper the salt, or the copper or chromium salts may be prepared in substance and used for dyeing fast shades.

The copper salt of the disazo dye obtained by coupling tetrazotised toluidine with Schaffer's acid (2-naphthol-6-sulphonic acid) is insoluble in water, oil, and benzene and cannot be obtained.[80]

The earlier experiments which showed that chromable dyes may be obtained from o-diazophenols,[81] have been extended to 4-nitronaphthalene 1-diazo-2-oxide, a very stable compound which possesses the remarkable property that coupling with the more reactive phenols, notably resorcinol, is facilitated by the presence of strong acids.[82] 1-Nitro-β-naphthol 1-azo-resorcinol dyes unmordanted wool in reddish brown shades, changing to violet when coppered or bluish black when chromed. 1-Nitro-β-naphthol which was prepared in the course of the investigation, couples readily with diazonium compounds producing azo colours which dye quite different shades from those obtained with similar dyes derived from the unnitrated naphthol, thus the dye derived from diazotised sulphanilic acid dyes wool in deep red shades quite unlike those obtained from Orange IV.

A brown azo-colouring matter is obtained by diazotising picramic acid, coupling with α-naphthylamine or nitrosing and coupling with salicylic acid.[83]

[78] Soc. Chem. Ind. Basle, Eng. Pat. 129782, J., 1919, 757A
[79] Soc. Chem. Ind. Basle, Eng. Pat. 126466, J., 1919, 457A
[80] A. E. Gessler, U.S. Pat. 1289368, J., 1919, 68A
[81] G. T. Morgan and J. W. Porter, Chem. Soc. Trans., 1915, 107, 645, J., 1915, 653.
[82] G. T. Morgan and E. D. Evans, Chem. Soc. Trans., 1919, 115, 1126; J., 1919, 893A.
[83] Butterworth-Judson Corporation, U.S. Pat. 1310533, J., 1919, 677A
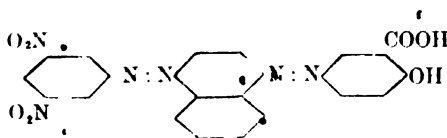
Amines of the general formula, $(NO_2)(5)\cdot(NH_2)(2)\cdot C_6H_3\cdot CO\cdot NR_2$, where R is an alkyl or aryl radicle, prepared by condensing nitroisatoic acid with secondary amines
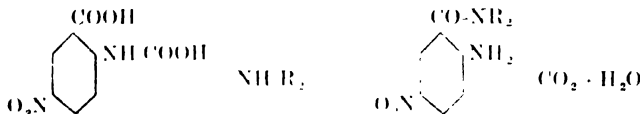
are diazotised and coupled with sulphonic acids and other derivatives of β-naphthylamine producing acid dyes which dye wool in level red to violet shades of good fastness to milling and light.[84]

By nitrating *m*-phenylenedithiolacetic acid (I), and treating the nitro derivative with hydrogen peroxide followed by reduction, sulphazone-6-sulphon-acetic acid (II) is formed. This compound couples with diazotised amines forming azo dyes,[85] such as 4-sulphonaphthalene-azo-sulphazon-6-sulphon-acetic acid (III) which dyes silk an old-gold shade stable to light and soap

I.   II.

III.
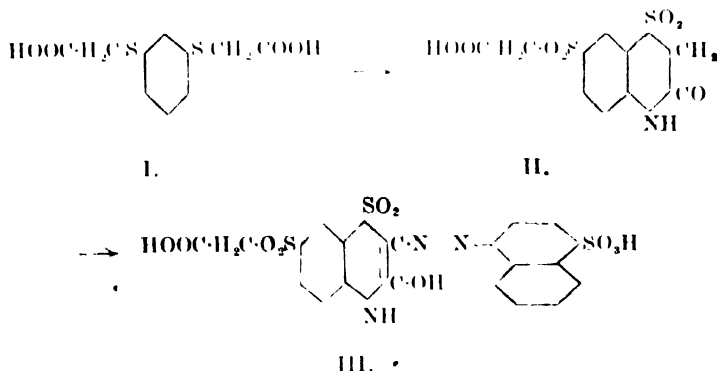
Azo dyes containing an asymmetric carbon atom are prepared by coupling the diazotised methyl- and ethyl-carbinols derived from *p*-aminobenzhydrol with various components,[86] for example :

[84] F. Bayer & Co., Ger. Pat. 309951 ; *J.*, 1919, 354A

[85] C. Finzi and N. Bottugheri, *Gazz. Chim. Ital.* 1918, 48, ii, 113.

[86] C. W. Porter and C. T. Hirst, *J. Amer. Chem. Soc.*, 1919, 41, 1264 ; *J.*, 1919, 756A.

$$\begin{array}{c} HO \diagdown \diagup C_2H_5 \\ \diagup C \diagdown \\ C_2H_5 \diagup \quad \diagdown C_6H_4 \cdot N \colon N \cdot C_6H_3(OH)SO_3H_2 \end{array}$$
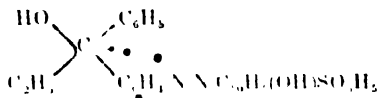
It is claimed that wool acts selectively on dyes of this type, the lævo- being absorbed to a greater extent than the dextro modification.

The Diazo Reaction

A study of the behaviour of certain hydrocarbons with diazonium compounds shows that, although ethylene and propylene will not couple under any conditions, butadiene and its derivatives, isoprene, piperylene, and β-dimethylbutadiene [87] couple readily with negatively substituted diazonium compounds with elimination of water, forming azo compounds of the type CH$_2$·CH·CH·CH·N:N·C$_6$H$_4$NO$_2$. The azo compounds are orange-yellow in colour, are reduced to hydrazo compounds, and combine with four atoms of bromine which shows that the double bonds in the hydrocarbon remain unaffected by the coupling.

ANTHRAQUINONE VAT DYES

Pure anthraquinone is obtained by the reduction of the solid commercial product with finely divided iron and a hot alkaline solution; the mixture is filtered and the filtrate oxidised.[88]

The yield of β-aminoanthraquinone obtained by heating anthraquinone-β-monosulphonic acid with ammonia under pressure, is increased by the addition of calcium chloride to the mixture together with ammonium chloride, sodium chloride, or magnesium chloride.[89]

An interesting method has been developed for the synthesis of **β-anthrimides**, which are valuable vat dyes.[90] For example, 1-chloro-2-**amino-anthraquinone** is diazotised and treated with an excess of ammonia, whereby dichlorobisdiazoanthraquinone amide (I) is formed, and is converted by boiling with nitrobenzene and benzoyl chloride into 1,1'-dichloro-2,2'-dianthrimide (II), which dyes cotton in orange-yellow shades from a reddish-brown vat.

I.
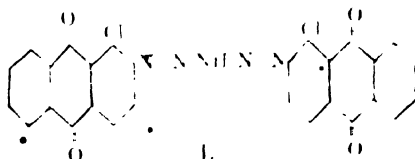
[87] K. H. Meyer, *Ber.*, 1919, **52**, 1468.
[88] H. F. Lewis and H. R. Gibbs, U.S. Pat. 1293610, *J.*, 1919, 280A.
[89] J. R. Geigy, Eng. Pat. 127223, *J.*, 1919, 529A.
[90] Meister, Lucius, and Brüning, Ger. Pat. 308696, *J.*, 1919, 37A.
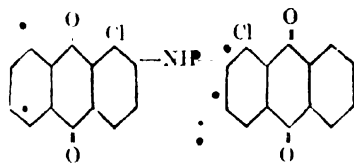
II.

The desire to improve the Indanthrene melt continues to attract attention   N-dihydro-1 2 2'-1'-anthraquinone-azine is obtained in a purer condition by the addition of potassium chlorate to the molten caustic potash prior to the addition of the β-aminoanthraquinone.[91] On the other hand, an improvement in the reaction also results from the addition to the molten caustic potash of a sugar such as dextrose prior to the addition of the β-aminoanthraquinone.[92] In a similar manner, the formation of by-product   due to excessive oxidation during the production of dibenzanthrone by the alkaline fusion of benzanthrone, is avoided by the addition of sugars to the melt.[93]

When N-dihydro-1 2 2'-1'-anthraquinone-azine is chlorinated in presence of sulphuric acid or chlorosulphonic acid, a certain amount of oxidation occurs with formation of the azine. Such oxidation is avoided by chlorinating a suspension of the compound with an excess of chlorine in a non aqueous inorganic liquid containing halogen, such as sulphuryl chloride, antimony pentachloride, sulphur chloride, thionyl chloride, phosphorus oxychloride, or bromine[94] The pro-ducts of the reaction are tri- and tetrachloro derivatives which are reduced readily and dye cotton in shades fast to chlorine. Chlorin-ated products free from bromine are obtained by chlorinating a sus-pension in bromine, but a bromo derivative which is difficult to reduce is obtained by the prolonged suspension of Indanthrene in bromine.

Anthraquinone-1-sulphonic chloride is a very reactive substance[95] which forms anthraquinone-1-sulphohydrazide (I) with hydrazine hydrate, and with ammonia it forms the sulphonamide, which loses water producing the anhydride anthraquinone-1-sulphanide (II).

[91] J. Morton, A G Dandridge, and Morton Sundour Fabrics, Ltd., Eng. Pat. 126112 ; J., 1919, 406A

[92] A. G. Perkin, Eng Pat 126764 , J , 1919, 458A

[93] A. G. Perkin, Eng. Pat 126765 ; J , 1919, 458A

[94] Soc. Chem. Ind. Basle, Eng. Pat. 113783 ; J., 1919, 130A.

[95] F. Ullmann and P. Kertesz, Ber., 1919, 52, 545.

I.   II.
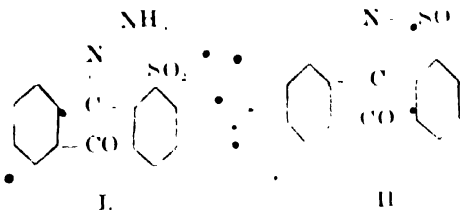
5-Nitro-anthraquinone-1-sulphamide, prepared by the reaction of ammonia on the corresponding nitro-sulphonic chloride, forms a dark green vat from which the fibre is dyed in pale red shades.

Thiazole condensation products, to be used in the production of vat dyes, are formed by the action of alkali sulphides on ω-halogen substituted acidylaminoanthraquinones.[96] Thus
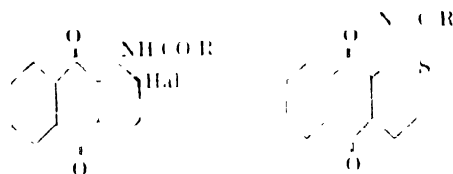
The azo-methine condensation product, obtained by heating 1-amino-2-methylanthraquinone with aromatic nitro compounds, alone or with addition of primary aromatic amines, in presence of alkalis, are converted into 1-aminoanthraquinone-2-aldehyde by treatment with acids.[97] When this aldehyde or the intermediate azo-methine compound is condensed with hydrazine a product is obtained which dyes cotton from the vat in claret red shades of very good fastness.[98]

The synthesis of benzanthrone derivatives referred to in a former report [99] has been followed by a study of rearrangement reactions in the anthraquinone-fluorenone series.[100] Anthraquinone-2'-1-fluorenone (IV) is prepared according to the scheme
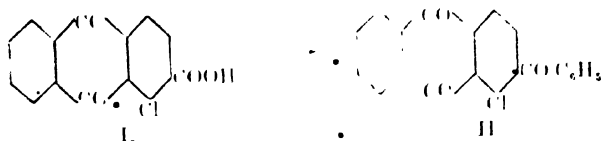
I.   II.

[95] Meister, Lucius, und Brüning Ger Pat. 311900, J 1919, 676a.
[97] G Kalischer, U S Pat 1285720, J, 1919, 130a
[98] G Kalischer, U S Pat 1285727, J, 1919, 130a
[99] Ann. Repts, 1917, 141.
[100] A. Schaarschmidt and J Herzenberg Ber, 1918, 51, 1230.
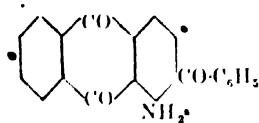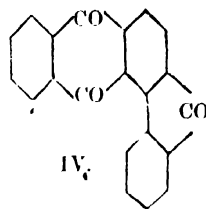
III.   IV.

It is not converted into 1 o carboxyphenylanthraquinone (V) by fusion with caustic potash at 220° 230° C., as might be expected from the behaviour of allochrys-oketone carboxylic acid, but a mixture of acids is obtained containing the dicarboxylic acid (VI) as is shown by the formation of anthraquinone 2 3 fluorenone (VII) on treatment with concentrated sulphuric acid
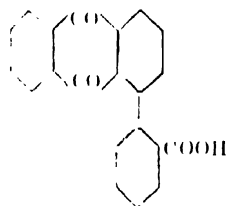
V.
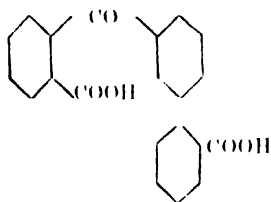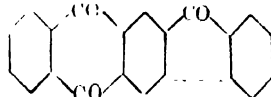
VI.   VII.

INDIGOID VAT DYES.

In the course of an investigation of derivatives of the indole and indigotin groups, substituted at the nitrogen atom,[101] it is shown that 1-hydroxy-3-benzoyloxy-2-thio-oxindole [102] reacts as a thiol (I) with phenylhydrazine, forming 3-benzoyl-2-thioloxindole-1-phenylhydrazone hydrate (II) · the sulphur is eliminated from this compound by treatment with N/2 sodium hydroxide, forming 1.1'-bisphenylhydrazinoindigotin (III), which is not a vat dye, but a true vat dye, indigotin-1.1'-imide (IV), may be obtained from it :—

101 A. Albert, Annalen, 1918, 416, 246 ; J., 1919, 37A.
102 A. Albert, Ber., 1915, 48, 474 ; J , 1915, 829.

$$NO_2 \diagdown \begin{matrix} C_6H_4 \\ C(SH) \end{matrix} \diagup CH\cdot O\cdot CO\cdot C_6H_5$$

I

$$\longrightarrow C_6H_5\cdot NH\cdot NH\cdot N(OH) \begin{matrix} C_6H_4 \\ C(SH) \end{matrix} \diagup CH\cdot O\cdot CO\cdot C_6H_5$$

II

$$\longrightarrow C_6H_4 \diagup \begin{matrix} CO \\ N(NH\cdot NH\cdot C_6H_5 \end{matrix} \qquad \begin{matrix} CO \\ N\cdot NH\cdot NH\cdot C_6H_5) \end{matrix} C_6H_4$$

III

$$\begin{matrix} CO\cdot C \quad C\cdot CO \\ | \quad \quad | \\ C_6H_4\cdot N\cdot NH\cdot N\quad C_6H_4 \end{matrix}$$

IV
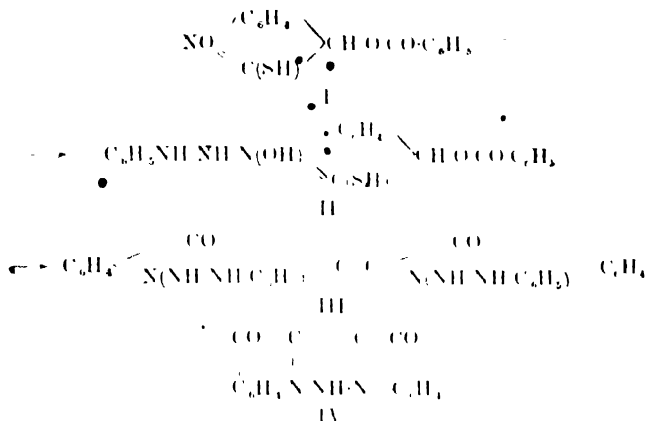
An interesting synthesis of isatin and its derivatives has been developed, dependent on the intermediate formation of iso-nitroso-acetanilide (I) or its N-mono-substitution products or ring-substituted products, which readily condense with sulphuric acid with formation of first the isatin β-imine (II) and then the isatin (III) in good yield.[104] The case of isatin itself may be formulated.

$$NH_2OH + CCl_3CH(OH)_2 = CCl_3\cdot CH\cdot N\cdot OH + 2H_2O$$
$$CCl_3\cdot CH\cdot N\cdot OH + NH_2\cdot C_6H_5 + H_2O = C_6H_5\cdot NH\cdot CO\cdot CH\cdot N\cdot OH$$

I

$$= C_6H_4 \diagup \begin{matrix} NH \\ C(NH) \end{matrix} \diagdown CO + H_2O = C_6H_4 \diagup \begin{matrix} N \\ CO \end{matrix} \diagdown C\cdot OH + NH_3$$

II   III
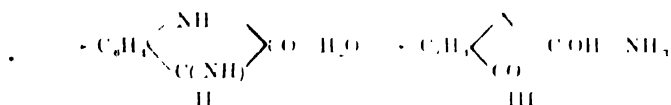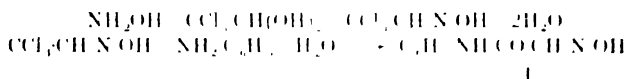
Oxidation converts O-acetylindoxyl into indirubin, but on the other hand, N-acetylindoxyl is converted by oxidation into the red diacetyl indigotin. Consequently, in the latter compound, both acetyl groups are attached to nitrogen, which may explain the great difference in colour from that of indigotin.[104]

A large number of substituted indirubins have been prepared and examined during the year under review. A particularly simple method for their preparation consists in the addition of the technical melt of phenylglycine to an acetic acid solution of the isatin warmed on the water-bath,[105] for example, 2-indoxyl-2-(5-methyl-1-7-α-methyltri-

[104] T. Sandmeyer, *Helv. Chim. Acta*, 1919, **2**, 234; *J.*, 1919, 150A. J. R. Geigy, Eng. Pat. 128122, Ger. Pat. 313525; *J.*, 1919, 624A.

[104] D. Vorländer and J. von Pfeiffer, *Ber.*, 1919, **52**, 325; *J.*, 1919, 456A.

[105] J. Martinet, *Comptes rend.*, 1919, **169**, 183; *J.*, 1919, 676A.

methylene) indole (III) is obtained in this manner from 5-methyl-1.7-
α-methyltrimethylene-isatin (I) and indoxyl (II) :—

H₃C ... CO / CO / N / H₂C ... CH-CH₃ / CH₂

I.

CH₂ ... CO / NH

II.

H₃C ... C—C / CO / NH / N / H₃C ... CH-CH₃ / CH₂

III.
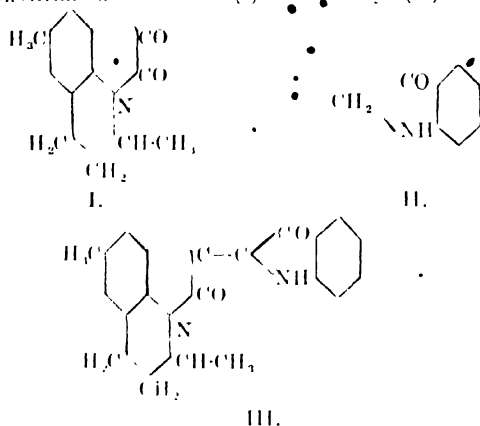
The substituted indirubins form pale yellow vats with alkaline
hydrosulphite, which dye wool and silk readily, but show little affinity
for cotton. Sulphines, which dye animal fibres in shades similar to
those of the parent indirubins, are obtained by warming the indirubin
with sulphuric acid.

Dyes of the Indigo Yellow series [106] are reduced by hydrosulphite
and caustic alkali to red vats which are very sensitive to oxidation
by air. On the other hand, by effecting the reduction with hydro-
sulphite in presence of alkali carbonates, insoluble free leuco-compounds
(phenols) are formed which are characterised by exceptional stability
to air and are well-suited, consequently, for permanent stable prepara-
tions. [107]

The sulphonation which occurs during the bromination of indigo
and its homologues in chlorsulphonic acid solution, is avoided by carry-
ing out the reaction in presence of phosphoric anhydride. [108] The
hydrogen bromide produced during the reaction is oxidised with
formation of water, which combines with the phosphoric anhydride,
and consequently, as no nascent sulphuric acid is formed, no sulphona-
tion takes place.

SULPHIDE DYES.

The opinion has been advanced that all constitutional formulæ at
present proposed for sulphide dyes are improbable in the case of highly
sulphurised products, because sufficient consideration has not been given

[106] Soc. Chem. Ind. Basle, U.S. Pat. 994288; J., 1911, 886.
[107] Meister, Lucius, und Brüning, Ger. Pat. 312601; J., 1919, 757A.
[108] Soc. Chim. des Usines du Rhone, Eng. Pat. 119860; J., 1919, 757A.

to the important part played by the colloidal and labile thiozone sulphur on the constitution and properties of the dye.[109] The problem of the constitution of sulphide dyes is aggravated by their colloidal nature and the natural adsorption exerted between the dye and colloidal sulphur. It is thought that the dye-skeleton is not affected materially, and the mother substance of the dye remains when the labile thiozone sulphur and colloidal sulphur amounting to some 20–25% of the total sulphur content are removed from black sulphide dyes by successive oxidation and extraction with solvents. A dye purified in this manner is more readily soluble in sodium sulphide or alkali hydrosulphite than the original dye, but exhibits markedly inferior dyeing properties.

Several additions have been made to the already large class of sulphide dyes during the year under review.

The investigation of cymene, recovered as a by-product from the sulphite-cellulose process, has attracted attention from several points of view recently. Cymene is converted by successive oxidation and nitration into mono- and dinitro-p-toluic acids which yield a brown sulphide dye by fusion with alkali polysulphides.[110]

The application of acenaphthene in dyestuff manufacture, which has been confined formerly to the production of vat dyes, has now been extended to the production of sulphide dyes. A reddish brown sulphide dye, for which extraordinary fastness to washing and chlorine is claimed, is obtained by heating a mixture of 1 part of acenaphthene with $3\frac{1}{2}$ parts of sulphur at 250–300° C.[111]

Blue sulphide dyes are obtained by the action of the polysulphide melt on a mixture of leuco-indophenols and p-nitro-amino-compounds of the benzene series which do not contain hydroxyl groups. The dyes prepared in this manner are superior in fastness, purity of shade, and intensity to those obtained without the addition of the nonhydroxylated benzene compound.[112]

Dichloronitrodiphenylamine, produced by condensing 1.2.4.5-trichloronitrobenzene with aniline, when condensed with p-nitrosophenol in sulphuric acid solution and reduced forms 4-p-hydroxyphenylamino-2-amino-4.5-dichlorodiphenylamine

which is converted into a blue sulphide dye by heating with alkali polysulphides.[113]

[109] W. Zanker, Z. angew. Chem., 1919, 32, 49; J., 1919, 248A.
[110] B. F. Halvorsen and O. Horbye, Eng. Pat. 128999; J., 1919, 623A.
[111] M. Wyler, and Levinstein Ltd., Eng. Pat. 124589; J., 1919, 318A.
[112] Chemical Works, formerly Sandoz, Eng. Pat. 129482; U.S. Pat. 1302674; J., 1919, 530A.
[113] L'Air Liquide, Eng. Pat. 118403; J., 1919, 677A.

Blue-black sulphide dyes are produced by heating an azo dye, derived from diazotised picramic acid coupled with a cresol or cresols, with free cresol, sulphur, and sodium sulphide.[114]

NATURAL DYES.

Efforts to relieve the shortage in dyes have resulted in attracting increased attention to natural dyes in all parts of the world. Promising results have been obtained in India in dyeing trials with the powdered dye obtained from red sanderswood, and experiments have been made also in the extraction of a yellow colouring matter from the flowers of *Butea frondosa*, and of annatto from the seeds of *Bixa orellana*.[115]

Investigation has shown that some sixty varieties of Japanese trees and twelve varieties of plants are of value as the raw material for dyes.[116]

The dyeing properties, on various mordants, of the colouring matter extracted from the bark of species of *Coprosoma* have been studied,[117] and it is claimed that extracts of the bark and roots of certain South African trees dye a variety of shades from pink to black.[118]

The fact that the colouring matter of Persian berries, xanthorhamnin, is a glucoside, is utilised in the manufacture of lakes, for, according to the temperature and duration of the reaction, it is hydrolysed to a greater or less extent into rhamnetin and rhamnose by the acidity of the salts used.[119] The canary-yellow lake of xanthorhamnin is obtained from an extract of Persian berries, tin salts, potash alum, and caustic soda at 50° C., but the dark orange lake of rhamnetin results from prolonged reaction at 100° C., whilst at intermediate temperatures (50°–100° C.) the shades obtained correspond to a definite mixture of the lakes of xanthorhamnin and rhamnetin. Similar results are obtained with quercitrin.

Reference has been made in a former report[120] to the synthesis of curcumin. Experiments carried out prior to the publication of this synthesis are in entire agreement with the formula of diferuloylmethane proposed, and, moreover, the relationship shown in the following scheme has been established:[121]

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[114] Brotherton & Co., E. F. Ehrhardt, and W. W. Kay, Eng. Pat. 127143; *J.*, 1919, 529A.

[115] *Ninth Ann Rep Ind. Inst. of Science, Bangalore*, *J.*, 1919, 4R.

[116] *Bd of Trade J.*, Jan. 9, 1919. *J.*, 1919, 16R

[117] B. C. Aston, *N.Z. J. Sci. Tech.*, 1918, 1, 264, 346, *J.*, 1919, 169A.

[118] R. Harbottle and S. Silverton, Eng. Pat. 126742; *J.*, 1919, 458A.

[119] J. Zubelin, *Bull. Soc. Ind. Mulhouse*, 1914, 84, 571; *J.*, 1919, 712A.

[120] *Ann. Repts.*, 1918. 3, 111.

[121] P. C. Ghosh, *Chem. Soc. Trans.*, 1919. 115, 592, *J.*, 1919, 354A.

Dicarbethoxycurcumin.   Curcumin.

Diacetyl compound (m.pt. 254° C.).

Dicarbethoxyisocurcumin   -   Isocurcumin.

Consequently the suggestion that curcumin and isocurcumin are geometrical isomerides [122] is contradicted.

As a logical consequence of the conditions prevailing during the war, natural indigo has received a new lease of life. The area under cultivation in India has increased considerably [123] and many improvements in methods of cultivation and extraction are foreshadowed, which may allow more effective competition with synthetic indigotin in the future; [124] the use of phosphatic manures, for example, not only increases the yield of green plant per acre but produces, in addition, a plant of superior quality. [125]

A rapid method for the preparation of indigo in a yield of 70-80% from any species of plant has been developed. [126] The fresh leaves of the plant are extracted with water, the impurities are precipitated with slaked lime, removed by filtration, and the filtrate is evaporated to a syrup and extracted with acetone. The acetone is removed, and the crude indican hydrate which separates on freezing, is dissolved in alcohol, and on addition of benzene to the solution, pure anhydrous indican crystallises out.

The native indigo plant of West Africa, which is cultivated in Southern Nigeria, yields indigo containing 56% indigotin, when subjected to a similar treatment to that given in India. This figure compares well with Bengal indigo, but the yield is much less than that obtained in India when the calculation is made on the weight of green plant. [127]

[122] G. Heller, Ber., 1914, 47, 887; J., 1914, 644.
[123] J., 1919, 300B.
[124] J., 1919, 119B.
[125] W. A. Davis, Agric. J. India, 1919, 14, 21; J., 1919, 248A.
[126] B. M. Amin, Agric. Res. Inst. Pusa Indigo Pub. 1., J., 1919, 154A.
[127] Bull. Imp. Inst., 1919, 17, 31; J., 1919, 293B.

FIBRES, TEXTILES, CELLULOSE, AND PAPER.

By SIDNEY S. NAPPER, F.I.C., A.C.G.I.

THE difficulties under which industry is being carried on are reflected in the character of the publications dealing with this section as mentioned by J. F. Briggs last year, but the improvement in the output of research work of the best class has hardly been maintained. However, there have been signs of revived activity recently. Research Associations have been established in the principal textile industries, and a quantity of interesting work is being undertaken in various laboratories, which has not yet reached the stage of publication.

FIBRES AND TEXTILES

Cotton

A most striking addition to our knowledge of the structure of the cotton fibre has been contributed by W. L. Balls,[1] who, by hydration of cellulose according to Cross and Bevan's partial xanthation process, has obtained a swelling of the fibre which on microscopic examination exhibits well-defined zones corresponding to rings of growth during the day and night, the latter being the active period. He finds that up to the twenty-sixth day there is very little evidence of structure, but from then on to the fiftieth day the development of well-defined growth rings may be detected, together with the formation of pits in the cell wall and a tendency to produce the well-known twist in the fibre.

The Fine Cotton Spinners and Doublers Association, Ltd., with M. Cunningham and C. F. Cross,[2] claim that a considerable improvement in physical properties, such as elasticity, may be obtained by treatment of cotton with a solution of, for example, 9% caustic soda, which is too dilute to produce a mercerising effect.

Notwithstanding the large amount of work that has been carried out regarding the effect of mercerising and bleaching on the strength of cotton yarn, considerable uncertainty has existed as to the influence of these treatments on the strength of the individual fibre. R. S.

[1] *Proc. Roy. Soc.*, 1919, **B 90**, 542.
[2] Eng. Pat. 131212; *J.*, 1919, 759A.

Greenwood [3] finds that mercerising with or without tension causes an increase in yarn strength, but no alteration in fibre strength, while bleaching gives an increase in the yarn strength and a decrease in fibre strength. In the course of the work he found that in the yarn a much greater proportion (65%) is relieved of the available fibre strength than had been previously assumed (25%), and that the processes up to the stage of spun yarn have no deleterious effect on the individual fibres.

Several valuable papers have been published dealing with the purification of cotton which are of importance to the textile trade, and should also receive serious attention from the cellulose chemist. Although they may hardly be said to simplify the problem, the information contained in them is of extreme interest in connection with the question of obtaining a pure cellulose with a minimum of breakdown.

¶ Knecht and W. Hall,[4] in continuation of their earlier work, have investigated the purification of American and Egyptian cotton yarns. The effect of extraction with benzene, alcohol, water, ammonia, formic acid, hydrochloric acid, lime, and caustic soda was examined with special reference to the nitrogen content of the fibre. The total extract amounted to about 1%, and the nitrogen to 20 to 28% of the weight of the yarn. Boiling with lime or soap removed less than 50% of the nitrogen present, and no other single treatment was so successful as the caustic soda boil which removed 80%, but in order to reduce the proportion of nitrogen to less than 10% of the original figure it was necessary to bleach the yarn.

A paper by S. H. Higgins [5] on the same subject is generally in agreement with the above results, but the author concludes from the results of distillations with decinormal caustic soda solution, that the nitrogen is not all present in the form of protein, and calls attention to Hebden's observation [6] that 10% of the nitrogen cannot be removed by a soda boil. He deduces from this that a normally scoured cloth is not capable of forming chloramines on bleaching, because the protein constituents have been removed. The discussion of this question is usually dealt with in another section, but it should be noted that other forms of nitrogen are capable of forming similar compounds as is shown by the existence of phenylacetylchloroamines.

R. Haller [7] has studied the action of raw cottons on aqueous solutions of various salts. In some cases a negative adsorption was observed, that is the concentration of metallic base increased, indicating that the cotton was absorbing water in preference to the metallic hydroxide. The adsorption was found to increase with the purification of the

[3] J. Text. Inst., 1919, 10, 274; J., 1920, 10A.
[4] J. Soc. Dyers and Col., 1918, 34, 220; J., 1919, 7A.
[5] J. Soc. Dyers and Col., 1919, 35, 165; J., 1920, 16A.
[6] J. Ind. Eng. Chem., 1914, 6, 714; J., 1914, 950.
[7] Chem.-Zeit., 1918, 42, 597; J., 1919, 70A.

cotton, and the fact that bleaching lowered the adsorption indicated that the effect really was a function of the purification rather than of the accompanying breakdown or opening up of the cellulose molecule.

Wool.

S. A. Shorter [8] gives the result of further investigations into the influence of atmospheric moisture on electrical phenomena, and discusses the most suitable conditions for the operations of drawing and spinning In the case of worsted the recommended degrees of humidity are 70% and 50% respectively.

A. Woodmansey [9] gives the results of experiments on heating wool alone and in the presence of water. The effect of dry heat on wool, although appreciable at temperatures in the neighbourhood of 200.° C., is only slight up to 150°, the fall in strength in this latter case being about 3% At the higher temperatures it was found that the sulphur in the wool became oxidised to sulphate, and that nitrogen was split off in the form of ammonia. The presence of moisture caused the decomposition to become much more rapid

S A Shorter,[10] in an investigation of the scouring process, considers the relative merits of soap and alkali from the points of view of surface tension and emulsifying effect, and gives indications of the most desirable concentrations of these reagents He also makes suggestions as to the causes of exhaustion of a soap solution. Further light is thrown on this last problem by a paper of A. Woodmansey,[11] who gives figures for the amount of soap absorbed by wool from aqueous solutions. Various commercially scoured samples showed 0·20 1 03% of fatty acid. It was found that up to 3·6% of fatty acid might be absorbed by a cross-bred serge, and that a considerable quantity, from 0·11 to 0·91%, was retained after boiling in water. It also appeared that the alkali of the soap was absorbed to an even greater extent than the fatty acid Although this soap absorption is liable to lead to uneven dyeing, it is not entirely harmful as it is probably responsible for the superior feel of soap-scoured goods. A similar absorption phenomenon is probably the foundation of a patent of C. Bennert,[12] who claims that the use of acid decomposition products of albumin in washing wool gives a superior handle.

A. Kertesz [13] draws attention to the effect of weather in destroying wool fabrics, and claims that the biuret reaction may be employed to measure the degree of damage. Previous treatment with chromium

8 J. Text Inst , 1919, 10, 218 ; J., 1919, 677A.
9 J Soc Dyers and Col., 1918, 34, 227 ; J., 1919, 7A.
10 J. Soc. Dyers and Col , 1919, 35, 55 ; J., 1919, 249A.
11 J. Soc. Dyers and Col., 1919, 35, 169 ; J., 1920, 10A.
12 Gér. Pat 311542 ; J , 1919, 625A.
13 Z angew Chem.., 1919, 32, 168 ; J., 1919, 496A.

salts renders the wool much more resistant The principal cause of this effect appears to be active light rather than the presence of ozone or moisture The use of the above reaction is also advocated by M Becke,[14] who discusses the use of the biuret reaction for detecting the extent to which wool is broken down and dissolved by the different treatments to which it is subjected He claims that wool is likely to be damaged by dyeing in a bath containing sulphuric acid, as such a treatment renders it more sensitive to the attack by soap and alkaline reagents

W Herbig[15] finds that the xanthoproteic reaction of wool may be developed most strongly by bromine water

G G Jarman[16] describes an arrangement containing a hydro extractor for removing sand, etc., in wool scouring grease separation plants

Silk

Owing to the outbreak of war the publication in 1914 of a number of researches carried out under the direction of the Laboratoire d'Etudes de la Soie of Lyons was postponed and these have appeared this year in one volume containing the reports from 1911 to 1918 A short description is given of the results of experiments on the rearing at Lyons of *Atticora Myi* to the moth that produces Indian tusah, and papers on the following subject are printed in full: I, Silk cultivation in Bengal II, Variation in the moths of *Bombyx Mori* III, Reproductive organs of *Bombyx Mori* IV, Evolution of the satellus in the egg of the silk worm V and VI, Silk cultivation in Indo China VII, Silk cultivation in Morocco VIII, Silk producing lepidoptera The last paper describes 63 new varieties and is the eighth contribution on this subject completing the work of Dusuzeau, Sonthonnax, and Conte

J A Scheidt and W P Seon have gone very fully into the question of the grading and classification of raw silk and the latter has described an instrument for determining colour in raw silk thread[16]

F. Riesenfeld,[18] in discussing recent developments in the boiling-off process, states that saponin may be employed as the emulsifying agent, and that the use of enzymes has not been proved to be of advantage, but interest still continues to be taken in this process and T. Muta[19] describes a process of extracting from old worm pupae, moths, etc., an enzyme suitable for use in degumming silk

[14] *Farber-Zeit*, 1919, **30**, 104, 116, 128, J, 1919, 626a
[15] *Z. angew. Chem*, 1919, **32**, 120, J, 1919, 355a
[16] Eng Pat 118332
[17] *Misc. Pub. No. 19, U S Bureau of Standards*, 1918.
[18] *Farber-Zeit*, 1919, **30**, 13.
[19] U.S. Pats. 1296599, 1296600, 1296601, J, 1919, 358a, 383a

Flax, Hemp, and Miscellaneous Fibres.

The British Flax and Hemp Growers' Society, Ltd., give results of experiments by G. V. Eyre on the isolation of improved strains of flax seed for sowing purposes [20]. In the course of the work it appeared that *Linum usitatissimum* is to some extent subject to cross-pollination, and that the progeny exhibit the variations to be expected in accordance with the Mendelian theory. The continued selection and cultivation of plants producing tall branchless stems, under conditions preventing cross fertilisation, resulted in an improved strain showing greater uniformity and an increase in height of about ten inches.

R. Loeser [21] gives details of carrying out Rossi's process of retting flax with a culture of *B. comesii*. P. Kraus [22] discusses the retting of nettle stems in a solution of sodium bicarbonate. It appears that the principal agent in retarding bacterial retting is acidity, which in the process of water retting is removed by the current. A similar principle is involved in the process of E. L. Rinman,[23] who uses a caustic alkaline bath tempered by the presence of organic matter of an acid nature such as waste liquor from previous operations [24]

A. F. W. Brummer [25] obtains textile fibres from grasses, etc., by boiling with a 2% solution of sodium sulphide and then with alum or sodium thiosulphate containing a little acid. A. Sansome [26] describes a method of obtaining textile fibres from mulberry, and particulars are given [27] of a sample of "pita" fibre from Colombia which could be used as a substitute for sisal hemp.

Artificial Silk.

In spite of the increasing popularity of artificial silk, there appears to be a steady falling off in the amount of work published in connection with this subject.

Several new methods of preparing solutions of cellulose have appeared (see page 122), but their suitability for spinning artificial silk is doubtful and remains to be proved.

H. M. Specht [28] describes a combination of spinnerets. Courtaulds, Ltd., and J. E. Criggal [29] describe a method of making jets suitable for producing flat strips, and E. Dubot [30] claims a method of constructing spinning funnels.

[20] *Notes on Flax*, No. 7
[21] *Chem. Umschau*, 1918, **22**, 685; *J.*, 1919, 107A.
[22] *Z. angew. Chem.*, 1919, **32**, 25; *J.*, 1919, 169A.
[23] Eng. Pat. 128464; *J.*, 1919, 678A.
[24] Cf. B. S. Summers, *Ind. Repts.*, 1918, 120.
[25] Eng. Pat. 120199; *J.*, 1919, 458A.
[26] *Bull. Assoc. Ind. Lanera Ital*, 1918, **32**, 52.
[27] *Bull. Imp. Inst.*, 1918, **16**, 289.
[28] U.S. Pat. 1310509
[29] Eng. Pat. 127155; *J.*, 1919, 497A.
[30] Eng. Pat. 126263; *J.*, 1919, 407A.

These are practically all the contributions to the manufacturing process that have appeared working from other points of view. E. Formhals [31] contributes a method for distinguishing natural from artificial silk based on treatment with diazotised p-nitramine, which is of interest as it is claimed that the results are not masked in the case of a weighted and dyed material; and A. J. Cockatt and R. B. Forster [32] describe a hygrometer in which they make use of the expansion of an artificial silk fibre.

In an article on dyeing and finishing woven staple fibre, A. Winter [33] identifies this material in woollen goods by means of Naphthylamine Black EEF in acid solution.

Paper Yarns

The use of paper yarns for clothing textiles in Germany has followed the anticipated course, the lessened demand showing the failure of these substitutes for cotton. This is reflected in the diminished number of articles in popular and in scientific literature dealing with textile substitutes. In this connection it is of interest to note that A. G. Durgin [34] (U. S. Bureau of Standards) states that underclothing made from Japanese paper was, under a service test, that the articles gave 10% better protection against cold than did the standard equipment, and further that paper vests were used quite largely by aviators.

Attention has been called to the development of cellulose yarns made from pulp without taking it to the finished paper stage. The ribbons are formed from the suspension of cotton on the wire of the paper machine as in the Cross system, or on cylinder boards, as in the Turk system. The advantages claimed are superior strength, owing to the fibres being distributed longitudinally, good texture, and better behaviour in the dyeing baths [35].

In Japan interest is being taken in the weaving of paper with hemp, silk, and cotton. One such fabric recently described is composed of a silk warp and a paper weft, the latter being made from a *Broussonetia* fibre, and the operations conducted largely by hand [36]. Of Japanese origin also "Oriental panama," produced by coating twisted paper with solutions of nitrocellulose or celluloid, has found a market in this country, and in this connection a patent of A. Lehner [37] may be of interest.

[31] *Chem. Zeit.*, 1919, 43, 386; J., 1919, 624A.
[32] J., 1919, 95T.
[33] *Färber-Zeit.*, 1919, 30, 161; see J., 1919, 760A.
[34] *Pulp and Paper Mag.*, 1919, 25, 678.
[35] A. Kramer, *Monatschr. Textilind.*, 1918, 33, 81; J., 1919, 281A; A. Lein reber, *Kunststoffe*, 1918, 8, 234; J., 1919, 218A.
[36] *Paper*, 1919, 24, 971.
[37] Ger. Pat. 308561; J., 1919, 283A.

Balloon and Aeroplane Fabrics.

An interesting paper by B. D. Porritt [38] deals with the isolation and examination of textiles in rubber-proofed fabrics, and G. Martin and J. Wood [39] have described methods for the quantitative testing of rainproof cloths

J. D. Edwards [40] gives methods for and the results of testing the permeability of balloon fabrics by hydrogen, and in a paper with I. L. Moore [41] on the use of ultra-violet light for testing balloon fabrics, questions the constancy of the relation between the deterioration of these materials under the test and outdoor exposure   The radiation from the mercury arc varies greatly in intensity and character, and is very difficult to measure.   M. Entat,[42] however, is of the opinion that an exposure of from 2 to 4 hours to the ultra-violet rays gives analogous effects to an insolation of 30 days, and that the control is satisfactory.

A paper by G. B. Haven [43] gives the effect of moisture on the tensile strength of aircraft fabrics   Linen and heavy cotton materials gained 7% on the dry strength for each per cent. of added moisture, while cotton aeroplane fabrics similarly treated gained 3%.

E. D. Walen [44] discusses the methods used by the Bureau of Standards in developing the use of cotton fabric to substitute linen as wing fabric.   The method of covering the wings is described, together with details of testing doped and undoped fabrics.   He notes the smaller shrinkage of cotton fabrics on doping, but his statement that a well-made cotton fabric will resist more pressure than one of linen suggests that the ordinary tensile tests do not measure the bursting strength, as it appears from official specifications that the breaking strength of linen cloth weighing 4 oz. or less per yard is not less than 92 lb per inch warp and 95 lb per inch weft, while in the case of mercerised cotton fabric the figures for cloth weighing $1\frac{1}{2}$ oz. per square yard are 80 lb. for warp and weft.   A. Rusch [45] also gives some particulars of this mercerised fabric and its doping.

CELLULOSE.

No papers of outstanding importance have appeared during the year, but a number of interesting points have been placed on record.   The suggestion of W. Harrison [46] that the cellulose fibre itself may be regarded as the molecule should not pass without notice.   The views

38 J., 1919, 50T.
39 J., 1919, 84T.
40 U.S. Bureau of Standards, Tech. Paper 113 ; J., 1919, 169A.
41 Aerial Age Weekly, 1919, 9, 734.
42 Ann. Chim. Analyt., 1919, 1, 112 ; J. 1919, 409A.
43 Proc. Amer. Soc. Testing Materials,, 1918, 18, 380.
44 J. Amer. Soc. Mech. Eng., 1918 40, 933.
45 Text. World J., 1919, 56, 53.
46 Second Report on Colloid Chemistry, Brit. Assoc., 1919, 55.

of C. F. Cross, who regards it as a liquid system, tend in the same direction and, as expressed by Harrison and based on entirely different considerations, this idea is in harmony with the character to be expected of a material built up as closely the aggregation and condensation of soluble constituents of the plant juices, although it must not be interpreted too rigidly in view of the work of Balls on the structure of the cotton fibre.

No other hypothesis explains so well the alteration in chemical properties brought about by mechanical subdivision of the fibre, regarding which evidence is rapidly accumulating. For instance, C. G. Schwalbe and E. Becker [47] finds that in the production of a mucilage by mechanical means the copper reducing power of the cellulose is very considerably increased.

A similar change, also mechanically produced, is described by C. F. Cross and E. J. Bevan,[48] who give an account of their investigation of a sample of the cellulose powder received from M. Fort and referred to in last year's Report. Although its elementary composition corresponds exactly with the formula $C_6H_{10}O_5$, nearly 50%, is soluble in caustic soda and it appears to undergo considerable hydration with water with the formation of a flocculent curd as the temperature approaches the boiling-point. The specific volume is stated to be low. The method of formation and properties of the substance must be taken into account in arriving at any satisfactory picture of the cellulose molecule.

In many technical processes the hydration of cellulose is becoming of considerable importance. In a recent patent Cross and Bevan [49] describe a method of treatment with comparatively dilute alkali followed by carbon bisulphide, under conditions which fall short of the formation of a soluble xanthate. Such a process may have important applications in the mercerising and paper-making industries, and W. L. Balls (see p. 114) has already obtained most valuable scientific results from its application to the study of the physical structure of the cotton fibre.

A certain amount of confusion exists in botanical literature as to the nature of vegetable cuticle; it appears probable that it is not strictly composed of cellulose, the resistance of which to oxidation and the transpiration of water would not be sufficient. An interesting paper by the same authors [50] throws considerable light on the nature of this substance in the case of apple peel and raffia. The true cuticle which comprises 40% of the raffia, cannot be separated from the schlerenchyma by any chemical process without experiencing considerable attack by the reagents employed, and it appears to be a cellulose ester

[47] Z. angew. Chem., 1919, 32, 265; J., 1919, 858A.
[48] J. Soc. Dyers and Col., 1918, 34, 215; J., 1919, 7.
[49] Eng. Pat. 126174; J., 1919, 458A.
[50] J. Soc. Dyers and Col., 35, 70; J., 1919, 249A.

which yields on hydrolysis with alcoholic soda two acids, a fatty acid $C_{17}H_{.}O$, with one COOH and one OH group, and a resin acid containing 59·4% carbon and 10·0% hydrogen. The authors consider the lignification of the schlerenchyma to be "a secondary structural modification," but it is difficult to reconcile this with the fact that chlorination of the lignin appears only to take place in proportion to the extent to which the acid groups have been removed by alkaline hydrolysis.

P. E. C. Goissedet [51] describes a new reaction of cellulose. By heating cotton cellulose with phenyl isocyanate in pyridine a colloidal solution is obtained which on pouring into water gives a precipitate of cellulose phenylcarbamic ester.

Esters.

H Ost [52] gives a much needed comparative survey of the solubility of cellulose acetates. He points out that solubility in chloroform is characteristic of the pure tri-acetate, such as is obtained when using zinc chloride as catalyst, and that solubility in acetone is possessed by the partially hydrolysed products obtained on treating with water the mixed sulpho-acetates given by a free or combined sulphuric acid catalyst. Other hydrolysing agents such as acetic acid, aniline, and phenol produce similar results. A slight solubility in acetone is sometimes shown by the primary acetates, but this is not permanent and the material will not redissolve in this solvent.

G. Barr and L. S. Bircumshaw [53] comment on the unreliability of the Fehling test as a quantitative measure of the depolymerisation of cellulose in its conversion to acetate, and describe a case of the acid decomposition of dope on storage for two years. W. J. Stevenson [54] claims the use of bleached sulphite paper pulp in the manufacture of acetylcellulose. He employs glacial acetic acid and acetic anhydride with either zinc chloride, nitric acid, or dimethyl sulphate as a catalyst.

G. Leysteffer [55] gives an interesting study of the viscosity of acetone solutions of nitrocellulose prepared from cellulose obtained from pine wood. Nitrocelluloses from wood show lower viscosities than those made from cotton, and a high content of γ-cellulose gives an increase of viscosity in the resulting solution.

Solutions and Plastics

Solvents for cellulose continue to attract attention, but recent publications do not add much to our knowledge of the subject. The Zellstoff-

[51] Eng. Pat. 130277 ; J., 1919, 714A.

[52] Z. angew. Chem., 1919, 32, 70, 76, 82 , J., 1919, 355A.

[53] Advisory Committee for Aeronautics, Reports and Memoranda, 303 : J., 1919, 713A.

[54] Eng. Pat. 130029 ; J., 1919, 714A.

[55] Koll. Chem. Beih., 1918, 10, 145 ; J., 1919, 234A.

Fab. Waldhof and V. Hottenroth [56] claim mixtures of hydrochloric and sulphuric acid on almost exactly the same lines as the International Cellulose Co [57] W. Ogawa, S. Okabe, and I. Murata [58] employ a solution of zinc chloride, saturated at 60° C. and heat this with purified cotton to nearly 100° C. The degradation of the cellulose under these conditions must be considerable.

R. H. Clayton, J. Huebner, and H. L. Williams [59] claim the use of hot concentrated solutions of thiocyanates of calcium, manganese, strontium, or barium. Satisfactory results are also obtained by using a sparingly soluble thiocyanate such as mercuric thiocyanate dissolved in an aqueous solution of a soluble thiocyanate. A portion of the thiocyanate may be replaced by a salt such as calcium chloride, and the addition of 1% acetic acid is stated to be of advantage. A further claim by the same workers [60] covers the manufacture of "vulcanised fibre" and the like by passing paper through thiocyanate solutions and pressing together the resulting parchmentised sheets.

H. A. Levey [61] makes a plea for a method of incorporating cellulose nitrate with China wood oil and polymerising the latter by heat

A. Dubosc [62] reviews the colloidal behaviour of cellul==oid and gives a summary of its chemical and physical properties. He concludes that from the colloidal point of view cellulose acetate products are inferior to those from nitrocellulose.

A considerable number of patents relating to dope and doping have been published during the year. The principal directions in which work is being carried out are to diminish the rate of evaporation of the solvent, to soften the dope coating, and to reduce the rate of ageing of the dope before application.

Wood

In spite of the mass of work that has been carried out on this subject, it still appears that there is considerable doubt as to the proportions of cellulose, pentosan, and lignin, particularly in hard woods. C. G. Schwalbe [63] has drawn attention to the necessity for systematic investigation, and in a discussion of the methods available [64] points out some of the uncertainties that affect the determination of lignin. He proposes that the cellulose determined by Cross and Bevan's method should be corrected for the furfural value of the product and

[56] Ger. Pat. 306818, J. 1919, 434A
[57] Eng. Pat. 104173, J. 1918, 410A
[58] Eng. Pat. 102 027, J. 1919, 470
[59] Eng. Pat. 123784, J. 1919, 582A
[60] Eng. Pat. 124974, J. 1919, 458A
[61] U.S. Pat. 1295833, J. 1919, 557A
[62] Caoutchouc et Gutta Percha, 1919, 16, 9863, J. 1919, 531A
[63] Z. angew. Chem., 1918, 31, 193, J. 1918, 685A
[64] Z. angew. Chem., 1919, 32, 125, J. 1919, 407A

a further suggestion that may lead to progress is that the determination of the wood-gum figure should be abandoned in favour of the separation of the α-, β-, and γ-celluloses as practised by Cross and Bevan. In a paper with E. Becker, the same author [65] gives results of the analysis of the woody material from flax and hemp in comparison with spruce, and it is here that the limitations of the methods employed begin to appear as the proximate constituents add up to over 100%. The authors ascribe this to the method of determining lignin by extraction with 72% sulphuric acid and propose to reject the results obtained in this way.

The results of W. H. Dore,[66] working on the same lines, render this last conclusion open to question, as his figures, obtained by a similar method, are more consistent. A comparison of his results for cellulose with those of Schwalbe suggests that the figures of the latter for this substance may be too high owing to the presence of traces of lignin. It is unfortunate that neither of these authors determined both the lignin and pentosan in their cellulose. Dore's examination of his cellulose for residues of lignin was very thorough, and renders his work in this respect of special value, but as he determined the hemicelluloses by extraction with boiling 1% caustic soda solution and obtained figures of about 10%, it appears that his cellulose must have contained a considerable amount of undissolved pentosans. He is aware of this and follows Schorger in claiming that these substances should be regarded as cellulose, but his contention is not likely to meet with acceptance by the majority of workers in this field.

E. Heuser and C. Skioldebrand,[67] by two successive treatments with 42% hydrochloric acid, obtained 33·12% of lignin from spruce wood, as compared with Schwalbe and Becker's figure of 30%. The lignin prepared in this manner was subjected to destructive distillation and the gaseous and liquid products determined in comparison with those from the original wood and from purified wood cellulose.

Comparative tests have been made of such methods as the above, in which the cellulose is dissolved out from the wood and the residual lignin determined gravimetrically, by J. König and E. Becker,[68] who found that in the case of deciduous woods the hydrochloric acid methods give more consistent results than the sulphuric acid method. Coniferous and deciduous woods were investigated with regard to the percentages of cellulose, lignin, pentosan, and hexosan. The figures for cellulose are notably lower than those given in the earlier papers of Dore and of Schwalbe and Becker.

Employing the hydrochloric acid methods of lignin determination

[65] Z. angew. Chem., 1919, 32, 126 ; J., 1919, 408a.
[66] J. Ind. Eng. Chem., 1919, 11, 556 ; J., 1919, 496a.
[67] Z. angew. Chem., 1919, 32, 41 ; J., 1919, 215a.
[68] Z. angew. Chem., 1919, 32, 155 ; J., 1919, 530a.

described in the last paper. Schwalbe and Becker [?] give the results of the complete analysis of various woods, the totals of some of which show considerable variations from 100%, which indicates that the details of the methods still require perfecting. The figures for lignin in coniferous woods are fairly well established to be between 25 and 30%, but the latest figures of Schwalbe and Becker for deciduous woods, which average about 20%, are about 6% higher than those of Dore.

A method of lignin determination, which is reported as it is free from several objections common to the above processes, has been investigated by P. Waentig and W. Gierisch [?] who determined the weight of chlorine absorbed by the woody material. The lignin was separated by Willstatter and Zechmeister's hydrochloric acid method and the weight found corrected for its content of chlorine and ash; it was then subjected to the action of chlorine and the increase of weight determined. Their method applied to two typical materials gave:

Pine wood	.	.	28.0	14.50	43.2 43.7
Rye straw	.	.	19.1	14.17	30.5

A critical study of the subject is given. Schwalbe's suggestion of the need for standardisation and recent work confirms the importance of the various empirical constants such as methoxyl and acetic acid figures. A scheme which would give a reasonable accuracy in ash, ether alcohol soluble, water soluble, lignin, pentosan, and cellulose would add enormously to our knowledge of the composition of wood. Fairly satisfactory methods for the determination of these are given in the papers of Schorger and Schwalbe, with the exception of lignin, but the position with regard to this constituent is still most unsatisfactory.

A method on the lines of the previously mentioned process of Waentig and Gierisch offers advantages over the removal of the cellulose by the use of such powerful reagents as sulphuric and hydrochloric acids. This process at first sight does not appear to be any improvement on the phloroglucinol method of Cross, Bevan, and Briggs, [?] and some tests made under the direction of the writer indicate that the latter gives quite useful results. The difficulty in all methods of this class is to determine the ratio in which the reagent is absorbed by the lignin, because direct tests involve the previous separation of the lignin by one of the processes to which exception has been taken. In the case of spruce wood, neither the lignin-phloroglucinol ratio of Klason, 100:23.2, nor the figure of 100:27.5, given by Cross and Bevan, appears

[69] Z. angew. Chem., 1919, 32, 229; J., 1919, 624A.
[70] Z. angew. Chem., 1919, 32, 173; J., 1919, 530A.
[71] Chem. Zeit., 1907, 31, 725.

to give satisfactory results, and the evidence is increasing that there are
several lignins with different phloroglucinol ratios. C. F. Cross, for
instance, in the paper referred to on p. 121, finds that the lignin in raffia
combines with chlorine in a similar ratio to that established for jute,
but that it does not absorb phloroglucinol. The proportion of methoxyl
may also vary according to the particular lignin present, as P. Klason [72]
obtains from fir wood two lignin-sulphonates corresponding to lignins
of the composition $C_{29}H_{26}O_{11}$ and $C_{40}H_{42}O_{12}$, containing 12:3% and 17% of
CH_3O respectively. The latter of these he regards as a condensation
product of three molecules of hydroxyconiferyl alcohol with one of
coniferyl alcohol.

A paper by H. Pringsheim and H. Magnus [73] calls attention to
further differences that exist between lignins from various sources,
namely as regards the yield of acetic acid. This constituent is appar-
ently present in the form of ester groups, as it is removed by treatment
with cold alkali, and the authors claim that by acetylation the hydro-
lysed product can be converted into the original substance. Their
work also emphasises the objections to the acid processes for separating
lignin, as they find that the product obtained by Willstätter and Zech-
meister's method has lost acetyl groups and is therefore not identical
with the original material present in the wood, and supports the ideas
of Cross as against those of Klason, who takes no account of the acetic
acid in his suggested formulae.

It appears from the work recorded up to the present that the lignin
nucleus is not appreciably altered by separation with strong acids, but
in order to obtain the true percentage of lignin the figure obtained
in this manner should be corrected by addition of the acetic acid figure ;
there are also reasons for supposing that a further correction should
be made for a proportion of methoxyl groups split off during the
separation.

K. H. A. Melander [74] obtains, by salting out with sodium chloride, a
different product from that described by Klason. It contains loosely
bound sulphur dioxide, which raises the proportion of sulphur in the
naphthylamine salts up to one atom of sulphur to one of nitrogen,
instead of two atoms of sulphur to three of nitrogen as found by Klason.
The molecular weights of the original lignin-sulphonates are very close,
Melander finding 882–991 as compared with Klason's figure of 916,
but there is evidence which indicates that the product is a mixture of
substances of very similar composition.

The A.-G. für Zellstoff- und Papierfab. [75] have patented a method
for preparing lignin derivatives for industrial purposes. They hydro-

[72] *Ark. Kemi, Min., o. Geol.*, 1917, 6, 2: pp. ; *J.,* 1919, 570A.
[73] *Z. physiol. Chem.*, 1919, 105, 179 , *J.*, 1919, 714A.
[74] *Teknisk Tidskr.*, 1918, 10, 12 ; *J.*, 1919, 625A.
[75] Ger. Pat. 309551 ; *J.*, 1919, 218A.

lyse the wood by boiling with formic or acetic acid containing 0·5% to 0·7% of sulphuric acid, and on diluting with water obtain a phenolic substance of high molecular weight, the dissolved carbohydrates remaining in solution.

S. A. Mahood and D. E. Cable[16] have investigated the proportions of formic, acetic, and oxalic acids formed by soda-fusion of various woods. At 170° C. both formic and acetic acids are produced in approximately equal proportions of 10–15%. As the temperature is raised the yield of formic acid decreases and that of acetic and oxalic acids increases, the maxima of 20%, and 60% respectively being obtained at temperatures between 200 and 230 C.

PULP AND PAPER

The development of cellulose as a substitute for substances in common use during the war has proceeded to a surprising extent. From recent publications it appears that it has been used for sacks of all descriptions, driving belts, shoe laces, webbing, electric wire insulation, school and military knapsacks, sleeping bags, puttees, T.N.T. container linings, machine-gun belts, an explosive hand-grenade (U.S. Mark 3, 4 oz. T.N.T.), which is stated to have been distinguished more by moral effect than by offensive value, and an aeroplane with paper wings, but unfortunately it does not appear whether this machine ever flew, or what was its ultimate fate.

World wide interest still continues to be taken in the question of the supply of raw material, owing to the gradual destruction of the forests in so many countries, the enormous increase in printed matter, and the new uses for cellulose that are being developed. Native vegetable matter of all kinds has been the subject of experiment in Australia, Egypt, France, India, Japan, the Philippine Islands, Spain, and the United States.

At present the only pulp mills in Australia are those of the Queensland Pine Company, where a small quantity of pulp is made from waste wood of the hoop and bunya pines (*Araucaria cunninghami* and *A. bidwilli*), and a small mill near Cairns, where blady and other grasses are employed as raw material. The prospect of the source of future supplies has to be considered seriously, and the question is gone into at length by G. Lightfoot.[17] The question of using several Australian timbers had been previously considered by H. E. Surface, for the Tasmanian Government, who found that myrtle (*Fagus cunninghami*), swamp gum (*Eucalyptus regnans*), blue gum (*E. globulus*), and stringy bark (*E. obliqua*) gave rather poor yields of short fibre pulp which were not commercially profitable.

[16] *J. Ind. Eng. Chem.*, 1919, **11**, 651 ; *J.*, 1919, 655A.
[17] *No. 11 Bulletin Commonwealth Advisory Council of Science and Industry*; *J.*, 1919, 356A.

whether its price will allow it to compete with wood-pulp is not yet
settled.

Boiling.

The determination of the composition and choice of the most suitable
proportions for sulphite boiling liquor is dealt with by P. Klason,[85]
who discusses the analysis of fresh and partly-exhausted liquor and pro-
poses a method of determining the loosely bound sulphur dioxide in
the latter by treating with excess of alkali to convert it into sulphite,
then acidifying, and titrating with iodine. He also draws attention
to the complications caused by the accumulation of organic acids in
the liquor towards the end of the digestion. W. E. B. Baker[86] describes
the detailed precautions necessary in determining sulphur dioxide and
concludes that Winkler's method is preferable to that of Hohn.

S. E. Lunak[87] gives the results of experimental digestions of spruce
by the sulphite process. The effect of variations in combined and total
SO_2 was studied and also the effect of alteration of temperature ; 5%
total SO_2 and 1% combined SO_2 were found to be the lowest proportions
giving satisfactory results. Somewhat similar figures, namely 4·5%
total SO_2 and 0·9% combined SO_2, are recommended for an " easy-
bleaching " pulp by O. L. Berger,[88] who gives a detailed description
of the Morterud process of indirect cooking by forced circulation. He
claims that the proportion of sugar in the liquor may be raised to 1%
in this process as against 2·2% in the Ritter-Kellner method.

E. Morterud[89] claims adding the chemicals to the digester in concen-
trated form and then diluting with preheated water or waste digestion
liquor.

Methods of causing circulation within the digester are put forward
by A. G. Westad and E. L. Häag,[90] and E. Schauffelberger.[91]

Waste Liquor.

V. K. Krieble,[92] from the results of analysis of representative Cana-
dian sulphite liquors, concludes that the best samples contain as much
sugar as European liquors and should yield 1% by volume of alcohol.
His range of 20% to 28% of organic matter in the form of reducible
sugars is higher than that of 15–20% in previously published data.
He attributes the difference in the yield of sugar to its partial destruc-

[85] Pulp and Paper Mag., 1918, 16, 1015, 1037 ; J., 1919, 38A.

[86] Paper, 1919, 23, 164 ; J., 1919, 570A.

[87] U.S. Dept. Agric. Bull. 620 ; Pulp and Paper Mag., 1918, 16, 815, 837, 863.
889 ; J., 1919, 37A.

[88] Paper, 1919, 23, 104 ; J., 1919, 570A.

[89] U.S. Pat. 1299597 ; J., 1919, 459A.

[90] U.S. Pat. 1309267 ; J., 1919, 678A.

[91] Eng. Pat. 124676 ; J., 1919, 357A.

[92] Paper, 1919, 23, 153 ; J., 1919, 571A.

tion in the cook, and not to variations in the strength of cooking, or the relative proportions of spruce and balsam, etc. His results show that most of the sugar is produced before the end of the seventh hour and that after this time the temperature is of great importance; should it exceed 145° C. the yield is materially reduced, the fermentable sugars being the first to be destroyed.

In spite of the large output of literature on the subject of the preparation of alcohol from waste sulphite liquor it appears from a paper by E. C. Sherrard and G. W. Blanco [93] of the U.S. Forest Service that in 1918, when their research was commenced, there was only one plant in operation in the United States and that the yields were far from satisfactory. A considerable number of experimental fermentations were conducted on both the laboratory and manufacturing scale, with yeast acclimatised to sulphite liquor by two different methods; the difference in the results however does not appear to be very considerable when compared with the quantity of alcohol theoretically obtainable.

R. H. McKee [94] reduces the content of sulphur dioxide in the liquor to preferably 0.35 grm. per litre by various methods, brings the temperature to 27-28° C., and adds yeast. Air is then blown through while the fermentation is proceeding and the liquid distilled to separate the alcohol, alkali being added to fix the sulphur dioxide. He claims [95] the removal of injurious sulphur compounds with alternatively a soluble barium compound, barium carbonate, and barium sulphide and the regeneration of carbonate, etc., from the barium sulphate in the sludge. More recently [96] he states that the harmful action of sulphur dioxide upon yeast in inhibiting its growth is due to the absorption of oxygen by the sulphites and free sulphur dioxide. In his opinion therefore these substances are not yeast poisons, but act by bringing about oxygen starvation. To overcome this he bubbles air through the fermenting liquid as above and then distils direct.

H. Landmark [97] digests algae and kelp with dilute acids and uses the product as a yeast nutrient in sulphite liquor fermentation. The algae and kelp are rich in phosphorus and potassium and supply aminoacids, while the carbohydrates are fermentable.

Further developments have been recorded in the production of fuel by precipitation processes. R. W. Stæhlenert has improved upon his process as outlined in his first patents, a novel point being the introduction of air at a higher temperature so that oxidation and decomposition occur simultaneously. This, through hastening the speed of the reaction, eliminates the inhibition by traces of iron, zinc, manganese, etc. Other

[93] *Paper*, 1919, 24, 746.
[94] Eng. Pat. 120520, ; U.S. Pat. 1273392; *J.*, 1918, 600A.
[95] U.S. Pats. 1284739, 1284740; *J.*, 1919, 71A.
[96] *Paper*, 1919, 24, 584.
[97] *Tidskrift Kemi*, 1919, 16, 113; see *J.*, 1919, 859A.

yellow coloration is almost proportional to the intensity of the bleach-
ing, and that it is doubtful whether this is due to the formation of
oxycellulose, as determinations of the latter did not exhibit sufficient
difference to account for the results. • The suggestion is made that the
effect is due to a chlorination product, but some positive evidence
must be brought forward before this view is likely to be accepted.
The interesting observation was made that soda pulp, both bleached
and unbleached, is much more affected by heat than sulphite and
sulphate pulps. In connection with this problem reference may also
be made to a paper by A. B. Hitchens,[115] who discusses the influence
of various sizing materials on the yellowing of pure rag paper brought
about by the action of light.

Sizing and Filling Materials.

Many of the contributions that have appeared with reference to
rosin sizing do not call for serious notice ; one, however, by F. C. Clark
and A. G. Durgin [116] goes very thoroughly into the question of the
effect of various proportions of free and combined rosin in relation to
the proportions of alum and paper and describes the results of experi-
mental batches. O. Aschan [117] points out that as much as two-thirds of
the alum may be lost in the back water and urges the importance of
running the machine with circulation of the back water. J. A. De
Cew [118] proposes the use of sodium aluminate in rosin sizing and H.
Wandrowsky [119] eliminates the rosin altogether and precipitates the
alumina from the alkali aluminate by means of a metallic sulphate
such as magnesium sulphate.

E. Sutermeister [120] has studied the viscosity of coating mixtures ·
made with different samples of commercial casein. Sodium phosphate
gave the most fluid mixture and ammonia the thickest, but the relative
values of the different solvents that were tested appeared to vary with
the sample of casein under examination. The behaviour of china clay
and satin white in the casein solution was also investigated.

A very large number of substances has been proposed during the
year for producing hard waterproof boards or leathery material, but
space does not permit these to be referred to in detail. They include
coal tar soap ; non-drying oils mixed with soot, talc, graphite, etc. ;
sulphite liquor pitch ; cellulose broken down by bacterial action ;
formaldehyde-glue with and without filling agents ; vegetable matter
treated with alkali and then with a metallic salt ; linseed oil, casein,
and alumina ; wax and rosin. •

[115] Sci. Amer. Supp., Apr. 5, 1919. • ,
[116] Tech. Assoc. Pulp and Paper Industry, 1918. 48 ; J., 1919, 571A.
[117] Chem. Zentr., 1919, 90, II., 190 ; J., 1919. 357A.
[118] U.S. Pat. 1300357 ; J., 1919, 497A.
[119] Ger. Pat. 312594 ; J., 1919, 715A.   [120] Paper, 1919, 24, 217.

V. Voorhees and O. Kamm [121] publish a careful study of the estimation of starch in sized papers. They show that direct hydrolysis is liable to produce sugars from the pulp itself and that extraction of pulp with water gives a small amount of extract. This latter, however, is not sufficient to prevent the elaboration of an analytical method and they get very good results with papers of known starch content by extraction with dilute acetic acid, hydrolysis of the extract with dilute hydrochloric acid, and determination of the sugar by volumetric estimation with Fehling's solution

R. B. Roe [122] discusses the testing of clay for filling purposes and is of the opinion that there is no satisfactory test for "retention."

Waste Paper.

Although the demand for waste paper for pulping is said to be decreasing, processes continue to appear for removing ink from waste paper; these may be roughly grouped in two classes, viz., claims for methods of treatment with chemical agents as in the patents of W. M. Osborne [123] and T. Jesperson [124] and mechanical improvements in machinery for causing the separation of the pulp and colouring matter during beating, T. Jesperson [125] and Union Franç. des Papeteries. [126] The utilisation of waste waxed paper has also received attention. O. Kress and L. F. Hawley [127] describe experiments on the recovery of paraffined paper which show that treatment with steam does not completely remove the wax and that satisfactory results can be obtained by extraction with gasoline; M. S. Salmon [128] states that a factory at Nutfield in Surrey is now ready to start work on a similar system.

Testing

As in previous years, progress in the testing of paper is receiving special attention in the U.S.A. and several improvements in instruments for this purpose have been described. There appears to be a consensus of opinion that the Mullen bursting strength tester is not a satisfactory instrument while the Schopper tensile strength machine requires modification if it is to be used for tearing tests

J. D. Malcolmson [129] describes tests made with the Webb tester on flat and corrugated boards and speaks very highly of its indications.

[121] Paper, 1919, 24, 1091; J., 1919, 757A.
[122] J. Amer. Ceram. Soc., 1919, 2, 69; J., 1919, 282A.
[123] U.S. Pat. 1298779; J., 1919, 459A.
[124] U.S. Pat. 1311563; J., 1919, 714A.
[125] U.S. Pat. 1311564.
[126] Fr. Pat. 490150.
[127] J. Ind. Eng. Chem., 1919, 11, 227; J., 1919, 259A.
[128] J., 1919, 157B.
[129] J. Ind. Eng. Chem., 1919, 11, 133.

It appears to be a very practical instrument useful for all kinds of materials and can be employed for tensile as well as bursting tests.

E. O. Reed and F. P. Veitch [130] describe an impact tester for fibre boards, worked by means of a falling weight, which they claim gives more information as to the quality of the material than can be obtained by means of the Mullen bursting strength test.

H. N. Case [131] describes a paper tearing resistance tester in which a strip is partly cut through and then loaded with a gradually increasing weight until it tears. It is claimed that this detects differences which are not indicated by the Mullen and Schopper machines.

S. D. Wells [132] gives results of tests made with a modified Schopper tester and is of the opinion that a smaller, cheaper, and better instrument should be devised. He discusses the relation between bursting, tensile, and tearing tests, and in referring to the results described in the preceding paper expresses the opinion that they correspond very closely with those obtained with a Schopper instrument.

[130] *Paper*, 1919, **24**, 923 ; *J.*, 1919, 712A.
[131] *J. Ind. Eng. Chem*, 1919, **11**, 49 ; *J.*, 1919, 169A.
[132] *Paper*, 1919, **23**, 750.

BLEACHING, DYEING, PRINTING, AND FINISHING.

By S. H. Higgins, M.Sc.,

Head of Research Department Bleachers' Association, Ltd.

A RECENT report of the Department of Scientific and Industrial Research[1] shows that a number of research institutions have been formed and that a large amount of public money is being spent on these institutions. Previous to the war research was not regarded favourably in this country, but now there is the danger of going to the other extreme. Moreover, if results are not obtained, there is the possibility of public opinion receding to its former position, for already we hear that some private research associations, which were formed at the time of the greatest enthusiasm have ceased to exist and have incidentally provided food for ridicule by practical men. As pointed out in Annual Report, 1918 research institutes in different centres should obtain the assistance of chemists engaged in the different branches of industry of those centres in order to make the new work a success. The success of this new departure is a matter of life and death to chemists. They are therefore very keenly interested in the development and anxious to help in any way possible. Some years ago, the present writer, after visiting foreign technical schools devoted to the teaching of the branch of chemical industry treated in this section, expressed the opinion that our schools were in advance of any others in the world.[2] This statement was considered outrageous by many people at the time, but later we had a confirmation of this view,[3] and the war has emphasised the point. Now it must be a necessary part of any scheme of research that these splendid facilities be utilised. Further, the war has shown that students from our university schools of chemistry are as good as those turned out by the universities of any other countries, and these schools must come into the scheme. The universities must be the centres of pure research. In the present writer's opinion, the proper manner to support research and scientific instruction in this country is first of all to recognise that research pays in the long run, to support the universities with Government grants,

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[1] *J.*, 1919, 307a.   [2] S. H. Higgins, *J.*, 1910, 660.
[3] W. F. Reid, Presidential Address, *J.*, 1911, 849.

and to assist the technical instruction of employees engaged in industry. Special research institutes should act as clearing houses of investigations and places of meeting for research workers in order to further the association of industry and science.

The present writer [4] has made a plea for a re-classification of the celluloses, and now C. G. Schwalbe [5] states that the time is ripe for a re-investigation of all the standard raw materials of the textile and cellulose industries to compare the determinations of the ash, moisture, fat, wax and resin, cellulose, furfural, methylfurfural, and methoxyl. The results could be used for the classification and the evaluation of new and little-known materials. A large amount of work is at present being carried out on the composition of vegetable products, and this work will have a bearing on the use of vegetable products in industry.

C. G. Schwalbe [6] finds that on treating vegetable matter with acids, washing, drying, and extracting with volatile solvents, the treatment with the acid results in much more fat and wax being taken up by the solvent. This fact had, however, been previously discovered [7] and fully described as regards the behaviour of cotton and flax fibres.

BLEACHING.

E. Knecht and W. Hall [8] found that the lime boil removed about 2·1% of matter from cotton yarn, this matter being made up principally of mineral constituents and pectic acid. On evaporating the caustic soda extract of cotton a dark residue rich in nitrogen and phosphoric acid was obtained. The alcohol extract of cotton was mainly mineral and contained about 20% of potassium, while the water extract contained a similar proportion of that metal representing 0·4% on the weight of the original cotton.

The elimination of the nitrogen from cotton and flax fibres during bleaching has been investigated,[9] an attempt being made to compare the behaviour of the proteins of wheat with those of cotton and flax when distilled with caustic soda. Caustic soda removed a large proportion of the nitrogen, and lime not so much, but the usual lime, sour, ash treatment removed practically all of the protein nitrogen. Properly scoured cotton cannot therefore produce chloramines because it contains no appreciable amount of protein. The statement of Cross, Bevan, and Briggs [10] that the nitrogen constituents of fibres are extremely resistant to alkali boiling is not borne out by the results.

[4] *Annual Reports*, 1918, 149.
[5] Verein deuts. Chem., Sept., 1918. *Z. angew. Chem.*, 1918, **31**, 193; *J.*, 1918, 685A.
[6] Ger. Pat. 309555; *J.*, 1919, 295A.
[7] S. H. Higgins, *J.*, 1914, 902.
[8] *J. Soc. Dyers and Col.*, 1918, **34**, 220; *J.*, 1919, 7A.
[9] S. H. Higgins, *J. Soc. Dyers and Col.*, 1919, **35**, 165; *J.*, 1920, 16A.
[10] *J.*, 1908, **27**, 282.

Knecht and Hall[11] found that the caustic soda boil removed about 80% of the nitrogen from cotton, a lime boil and sour 53·1°$_0$, and hot soaping 17·5%. After the caustic boil, chemic, and sour, only 5·8% of the original nitrogen remained in the cotton. These figures agree very well with those previously obtained by J. C. Hebden,[12] and it has been pointed out [13] that it is difficult to state the nature of the residual nitrogen of cotton after the caustic soda boil. A second caustic boil does not remove it. In fact, the state in which nitrogen is present in cotton and flax fibres has by no means been elucidated. We are certainly not justified in assuming it to be all present as protein nitrogen. Knecht and Hall found that on extraction with benzene the nitrogen contents of the cotton were reduced, from 0·204 to 0·189% for American, and from 0·202 to 0·240°$_0$ for Egyptian cotton. The distillation with caustic soda previously described also points to the nitrogen not being present entirely as protein, and the figures for the analysis of the cotton fibre [14] giving nitrogen 0·34°$_0$ and protein only 1·50°$_0$ bear out this contention. These facts have a bearing on the discussion on the existence of chloroamines in bleaching operations.[15] J. F. Briggs [16] persists in the statement that the "chemical odours" of bleached fabrics are due to the presence of chloramines in spite of the fact that as regards wood,[17] cotton,[18] and flax,[19] there is no evidence of the existence of chloramines in bleaching operations. It is also significant to note that Knecht and Hall [20] found, on applying bleaching powder solution to cotton, that there was immediately a very big drop in the nitrogen contents of the cotton.

The effect of the bleaching process on the strength of cotton fibres has been investigated.[21] Very little work has been done in this matter since that of C. O'Neill in 1864. The machine used in the present investigation was the Schopper, the single fibres being held in position between two pieces of paper. The results show that the single fibres actually decreased 20°$_0$ in strength during the bleaching. Cotton yarn was again found to increase in strength, thus pointing to a greatly increased cohesion of the fibres in the yarn, possibly owing to the removal of the natural wax, which would tend to act as a lubricant.[22]

The use of a baryta and strontia in place of lime has been again

[11] *Loc. cit.*
[12] *J. Ind. Eng. Chem.*, 1914, **6**, 714.
[13] S. H. Higgins, *loc. cit.*
[14] *Bulletin No.* 33, *U S. Dept. Agric.*
[15] *Annual Reports*, 1918, 151.
[16] *J.*, 1918, 447R.
[17] C. G. Schwalbe, *Z. angew. Chem.*, 1908, **21**, 302.
[18] R. E. Crowther, *J Soc. Dyers and Col.*, 1913, **29**, 28.
[19] S. H. Higgins, *J. Soc. Dyers and Col.*, 1918, **35** 43.
[20] *Loc. cit.*
[21] R. S. Greenwood, *J. Text. Inst.*, 1919, **10**, 275; *J.*, 1920, 10A.
[22] See S. H. Higgins, *J.*, 1914, 702, and *Annual Reports*, 1918.

tested [23] for the boiling of cotton goods, with the result that no change from present procedure is recommended. Baryta was found to be inferior in action to lime, but strontia proved to have a much more rapid saponifying action ; it had the disadvantage, however, of higher cost and tendency to cause tendering, and could only be recommended for special work. M. Freiberger [24] describes a number of experiments on the bleaching of cotton cloth ,with various bleaching agents, and arrives at the conclusion that the addition of sodium carbonate to bleaching powder solution has up to a certain limit a beneficial effect on the bleaching action of the solution. This statement, however, is not in accordance with previously described experiments,[25] which showed that the addition of sodium carbonate to sodium hypochlorite had a small retarding effect on the bleaching action of the latter solution ; the introduction of hydroxyl ions hindered the hydrolysis of the hypochlorite and diminished the amount of hypochlorous acid present. Freiberger's statement that the replacement of calcium by sodium hypochlorite produces a less energetic bleaching action is not in accordance with the results previously mentioned.[26] If the calcium be precipitated exactly by sodium carbonate the bleaching liquor obtained has bleaching properties identical with those of the original bleaching powder solution. Freiberger again states his preference for warm hypochlorite solutions, which, he says, give more permanent whites, and if used strong deposit calcium carbonate in a fine powder instead of as a crust from cold solutions. His work seems to indicate that from a few laboratory trials he attempts to make broad generalisations to affect the whole bleaching industry. As previously mentioned,[27] his conclusions should be taken cum grano salis.

The bleaching of goods containing coloured stripes is performed [28] as effectually as possible with treatments less severe than those employed for white goods, low-pressure kiers being employed, the duration of the boil reduced, and soda ash instead of caustic soda used for the scouring. In the case of Turkey red stripes prolonged treatment with acid should be avoided, as the mordants are thereby loosened ; also the cloth should be well washed out of the chemic before being scoured. During the war, owing to the scarcity of fast colours there has been much trouble with the bleaching of cloth containing colours [29] ; sometimes even hot water has caused colours, which were stated to be fast, to run. The only remedy for this continual trouble is co-operation between the bleachers of the cloth and the yarn dyers.

[23] R. Weiss, Bull. Soc. Ind. Mulhouse, 1914, 84, 499 ; J., 1919, 715A.
[24] Färber-Zeit., 1919, 30, 89–94 ; J., 1919, 409A.
[25] S. H. Higgins, J. Soc. Dyers and Col., 1914, 30, 12.
[26] S. H. Higgins, Chem. Soc. Trans., 1912, 101, 222.
[27] Annual Reports, 1918.
[28] A. C. Walsh, J. Soc. Dyers and Col., 1919, 35, 35 ; J., 1919, 218A.
[29] See Annual Reports, 1917.

In order to maintain an approximately constant quantity of liquor in bleaching kiers, and at the same time to ensure circulation, the liquor is made to flow by gravitation into a separate receiver, then returned in a practically continuous flow into the upper part of kier, this flow being approximately commensurate with the rate of drainage.[30] In order to prevent mineral acids from acting on cotton they are neutralised by alkali, the excess of alkali being eliminated by adding a volatile organic acid.[31]

Cotton at different stages of the bleaching process has been found to show a variable negative adsorption for aluminium acetate from solution.[32] This negative adsorption decreases as the degree of purification of the cotton increases; cotton boiled with lime gave higher results than if boiled with caustic soda. Negative adsorption was most pronounced in the case of Egyptian cotton. Using aluminium sulphate solution positive adsorption was observed in all cases with raw cottons and with those which had been lime-boiled, on the other hand, the well scoured and fully bleached samples all showed negative adsorption, increasing generally with the degree of purification. Lead acetate showed in all cases a large positive adsorption, increasing with the degree of purification. Maximum adsorption in all cases seems to correspond with maximum purification of the cotton, but treatment with bleaching liquor appears to decrease the purity of the cellulose; at any rate, it lowers the adsorption values. It has, further, been shown [33] that bleached cotton wool when immersed in a solution of aluminium acetate for 24 hours adsorbs about 0·1% of alumina, half of which is fixed on the cotton.

Many widely advertised bleaching preparations are stated [34] to possess no bleaching power whatever, while others are excellent, bleaching fabrics quickly and without damage. Faults are not generally due to per-salts contained in the preparations but to adulterants. Persulphates should not be used. B. Haas [35] points out that in using powders containing peroxides, in order to cleanse the dirty parts, it is necessary to overtreat the cleaner parts; hence, tendering takes place. By previously exposing on the grass and subsequently using a weaker solution of the peroxide the tendering action is reduced, while a previous treatment with an alkali minimises the risk of acid stains causing a rapid evolution of oxygen from the peroxide and thus producing tender parts.[36]

[30] G. B. Flood, U.S. Pat. 1290156; *J.*, 1919, 171A.
[31] A. E. Jury, U.S. Pat. 1289803; *J.*, 1919, 132A.
[32] R. Haller, *Chem.-Zeit.*, 1918, 42, 597; *J.*, 1919, 70A.
[33] G. Durst, *Chem.-Zeit.*, 1919, 43, 374; *J.*, 1919, 626A.
[34] H. Kühl, *Chem.-Zeit.*, 1919, 43, 354; *J.*, 1919, 589A.
[35] *Chem.-Zeit.*, 1919, 43, 49; *J.*, 1919, 171A.
[36] S. H. Higgins, *J.*, 1911, 30, 188.

Jackson and Bros, Ltd., and J. R. Fish,[37] protect the use of an electric device to control the speed at which the fabric is wound on the batch rollers in their well-known open-width kier.

For the removal of stains produced by coffee, chocolate, wine, etc., the use of glycol or a mixture of glycol and water has been protected.[38] An apparatus for chlorinating water or alkaline solutions for use in bleaching has been described.[39]

Of interest to bleachers is the statement of A. N. Meldrum [40] that bleaching powder is more rapidly dried in desiccators by means of alkaline agents, such as sodium hydroxide and basic calcium chloride, the tendency of bleaching powder to lose available chlorine being much reduced by desiccation. Bleaching powder loses chlorine in addition to water during the drying process, and this chlorine is absorbed by the alkaline drying agents.

The loss of oxygen during the use of oxygen-yielding bleaching agents has been determined by drawing off the oxygen evolved.[41] The results obtained when using perborates show that 60–80% of the active oxygen escapes in the gaseous form ; but if soap be present the loss is under 12%, the greater part of the oxygen being absorbed by the oxidisable constituents of the soap. To determine the free alkali and alkali carbonate in hypochlorite solutions W. Mestrezat [42] adds sodium thiosulphate to destroy the hypochlorite, then titrates the alkali and alkali carbonate directly. From observations on their reactions E. Justin-Mueller [43] concludes that alkali hypochlorites and bleaching powder have similar chemical formulæ.

DYEING.

The relative merits of natural indigo and of artificial indigotin have often been discussed. It has been pointed out that synthetic indigotin is not indigo since the latter material is a mixture of substances containing about 70% of indigotin. The substances other than indigotin contained in the indigo have an influence in the dye-vat, and for producing heavy shades the natural article is preferred by dyers. On wool, natural indigo gives deeper, brighter, and rather redder shades than the synthetic product. The production of indigo in India has recently been carefully investigated and improved.[44] A revival of the industry in China is also recorded.[45]

[37] Eng. Pats. 129171 and 129532 ; J., 1919, 678A.
[38] Goldschmidt, A.-G., Ger. Pat. 306707 ; J., 1918, 688A.
[39] N. K. Turnbull and H. N. Morris, Eng. Pat. 122888 ; J., 1919, 219A.
[40] J., 1919, 80T.
[41] A. Grün and J. Jungmann, Chem.-Zeit., 1918, 42, 473 ; J., 1918, 729A.
[42] J. Pharm. Chim., 1919, 20, 9 ; J., 1919, 602A.
[43] J. Pharm. Chim., 1919, 20, 113 ; J., 1919, 761A.
[44] H. E. Armstrong, J., 1919, 119R.
[45] J., 1919, 127R.

The weakening of wool in the acid, alkaline, and chroming baths used in dyeing and scouring has recently received the attention of many chemists, and the Research Institute for the Woollen Industries has encouraged work on these lines in this country.   M. Becke [46] finds that 2% sulphuric acid has the least action on wool as regards the wool passing into solution and as regards the strength and elongation of the material, but the fastest colours were obtained on the wool in a bath containing 4–6% of the acid. Chroming only reduced the breaking strain, while caustic soda mainly acted as a sulphur-abstracting agent and, unlike sulphuric acid, does not show a strong hydrolytic action. He recommends the biuret reaction to determine the amount of wool which goes into solution, the reaction being capable of adaptation to control purposes in conjunction with the mechanical breaking strain and elongation tests.

Apparent differences in the shades of yarns of different twist which have been dyed together have been pointed out. [47] These differences are only noticed when the yarns are woven in the same piece and are due to the light falling on the different angles of the twists. Many beautiful effects, such as stripes, are produced in this way by combining yarns differently twisted. J. Roulhn [48] points out that textiles dyed with yellow shades generally became more orange with the application of heat ; on cooling the original shade generally returns. A dry atmosphere has the same effect as the stove, the heat only acting as a moisture-removing agent.   Recipes have been published for the dyeing of artificial silk [19] and of mixtures of artificial and natural silk.[50] Goods dyed with Chloranthrene Blue B D. (Indanthrene) on storing in the Manchester atmosphere became reddish at the folds. This was found not to be due to sulphur fumes ; the faulty material had been developed by chroming and soaping, and from these treatments the change in shade had resulted.[51] To avoid this trouble reduction by a weak hydrosulphite vat is suggested. Too high a temperature and too much acid in the chroming both tend to over-oxidation and greenish blues. The present writer remembers a case where a blue of this series turned green in the chemic but gave a royal blue on after-treating with hydrosulphite. The blue thus produced was preferred to another blue which was unaffected by the chemic, but this treatment with hydrosulphite means expense, and for white goods containing blue stripes or borders cannot be entertained.

H. Wieland [52] proposes to reduce di- and tri-arylmethane dyestuffs with hydrosulphite in alkaline solution and use the bath in the same way

[46] *Färber-Zeit.*, 1919, 80, 101, 116, 128 ; *J.*, 1919, 626A.
[47] *Text. Manfr.*, 1919, 45.   [49] *Text. Merc.*, 1919, 129.
[49] *Amer. Silk J.*, 1919, 55.   [50] C. M. Whittaker, *Dyer*, 1919, 88
[51] C. M. Whittaker, *Dyer*, 1919, 229.
[52] Ger. Pat. 306298 ; *J.*, 1919, 10A.

as in dyeing with vat dyestuffs. Instead of using β-naphthol for developing colours on cotton, β-naphthol sulphide is employed, which is non-volatile during drying and steaming, resists the action of air well, and forms insoluble salts with the heavy metals.[53]   A dyestuff which dyes cotton direct is produced by treating the solids of waste sulphite liquor with a small amount of naphthylamine and of nitric acid.[54]   The action of copper salts on azo dyes which have been developed on the fibre has been further investigated.[55]   The orange or red shades obtained with β-naphthol and diazotised amines may be converted to brown shades, by after-treatment with copper sulphate, only if the ortho-position to the amine is not occupied.   Copper acetate brings about the change if the ortho-position is occupied and the para free ; when both positions are occupied the treatment with copper salts has no effect except in the case of xylidine, olive shades then resulting. On using different salts to effect the exhaustion of benzopurpurine baths, the precipitating power of these salts is not connected with the atomic weights of the metals of the salts.[56]   A further patent for the production of aniline black on cotton has been taken out.[57]   Aniline salt is replaced by aniline metaphosphate in prussiate baths to give a black which develops slowly ; the development can be regulated by the addition of catalysts.

The tendering action of sulphur black dyestuffs is said to be due [58] to the free sulphur present on the fibre after dyeing. If this sulphur is allowed to remain it gradually oxidises in the air to produce sulphuric acid which tenders the fibre, but if it be oxidised by bichromate and the goods washed well before drying then no tendering subsequently results.

The use of cresol containing about 5% of water has been suggested as a solvent for dyestuffs in the *dry dyeing* of woollen fabrics. The shrinking action of the cresol on the wool can be reduced by diluting with a neutral solvent such as solvent naphtha.   Other solvents [59] are methylated spirit, ammonia and fatty acids, benzene soap and formic acid ; the concentrated solutions are diluted by an inert hydrocarbon. Basic dyestuffs for dry dyeing are dissolved in carbon tetrachloride,[60] to which alcohol may be added along with a specially prepared mordant, "gallo-oleate of ammonia."   The dye-bath is heated to 62·5° C.,

[53] A. Porai-Koschitz, Ger. Pat. 308909 ; J., 1919, 284A.

[54] Robeson Process Co., U.S. Pat. 1283296 ; J., 1919, 71A.

[55] P. A. Driessen, *Chem. Weekblad*, 1919, 16, 628.

[56] J. Böeseken, G. W. Tergau, and A. C. Bumendijk, *Proc. K. Akad. Wetensch.*, 1919, 21, 893 ; J., 1919, 497A.

[57] The Calico Printers' Association, Ltd., and E. A. Fourneaux, Eng. Pat. 126201 ; J., 1916, 460A.

[58] *Text. World J.*, 1919, 55.

[59] M. Fort, J. *Soc. Dyers and Col.*, 1918, 34, 226, 227 ; J., 1919, 9A.

[60] H. Hey, *J. Soc. Dyers and Col.*, 1919, 35, 12 ; J., 1919, 102A.

and an electric current is passed through the dye-liquor during the dyeing of silk and woollen articles.

The use of calcium antimony tartrate as a *mordant* has been protected.[61] The utility of titanium salts as mordants and stripping agents has been pointed out.[62] By steeping cloth in a solution of titanium chloride or sulphate and then exposing it to air, a deposit of TiO_2 is obtained. This deposit may be increased by preparing the cloth with Turkey red oil or tin, and a variety of fast brown shades are produced by combination with tannin and iron.[62] The process of mordanting cotton by impregnating with titanous chloride and exposing to air without the use of tannin has been protected.[64] G. Durst[65] finds that cotton wool absorbs about 0·09% of alumina from aluminium acetate, half of which is fixed on the cotton. A dark blue colour has recently been extensively dyed in India from myrobalan extract and iron sulphate; a black is produced by after-treatment with copper sulphate-logwood. The shades are easily and cheaply produced, but good washing is necessary after dyeing in order to get rid of free acid.[65] The use of extract of the bark, wood, roots, and leaves of the retama tree as a mordant and colouring agent has been protected.[66] A new process of chrome-mordanting wool[67] consists of treating the wool with the usual bichromate and sulphuric acid and then with a bath of sodium sulphite. The chromium is produced in a reduced state and increased fastness in subsequent dyeing is said to result. The well-known blue ethereal solution of perchromic anhydride has been suggested[67] for the " dry " chroming of animal fibres. After the ' dry " mordanting of the fibres, the " dry " dyeing is done in a cresol-petroleum bath as previously described.

As regards *dyeing machines*, a device for preventing irregularities in the tensions of warps in the warp dyeing machine has been protected.[68] Guide rollers are provided immediately before and after the squeezing rollers and are mounted on yielding bearings controlled by springs. In order to improve penetration during dyeing[69] the material is given a to-and-fro motion whilst immersed in the vat, and then an up-and-down motion.

Two papers on the *theory of dyeing* have appeared. F. Feigl[70] found that, in dyeing inorganic solids, such as calcium carbonate,

[61] V. Planté, Eng. Pat. 119881 ; *J.*, 1918, 765A.
[62] S. M. Hermann, U.S. Pat. 1307860 ; *J.*, 1919, 627A.
[63] J. Barnes, *J. Soc. Dyers and Col.*, 1919, 35, 59 ; *J.*, 1919, 250A.
[64] J. Barnes and P. Spence & Sons, Ltd., Eng. Pat. 131098 ; *J.*, 1919, 760A.
[65] *Dyer*, 1919, 43.
[66] R. H. and M. H. Vegas, Eng. Pat. 129761 ; *J.*, 1919, 760A
[67] M. Fort, *J. Soc. Dyers and Col.*, 1919, 35, 100 ; *J.*, 1919, 319A.
[68] J. Bright & Bros., Ltd., and J. Evans, Eng. Pat. 119173 ; *J.*, 1918, 688A
[69] F. F. Larivei, Eng. Pat. 120648 , *J.*, 1919, 71A.
[70] *Oesterr. Chem.-Zeit.*, 1919, 22, 36, 42 ; *J.*, 1919, 569A

adsorption of the dyestuff only occurred usually in the case of dyestuffs which formed colloidal solutions. The dyestuffs remaining in the solid after washing with hot water were fast to light, air, washing with alkalis, and prolonged agitation with water. The dyed substances appeared quite homogeneous under the microscope, and the intensity of the colour depended on the size of the particles of the solid used, the duration of the dyeing, and the electrolytes present in solution. The results offer some support to the mechanical theory of dyeing and remind the present writer of the time when he produced beautiful dyeings of Turkey-red and other well-known colours on a series of inert inorganic solids. These dyed solids behaved in precisely the same manner towards washing, reagents, etc., as did cotton dyed in the same way. R. Haller [71] brings further evidence in support of his explanation of the dyeing process from the colloid standpoint. When cotton is immersed in tannin solution, the tannin, being highly dispersed, penetrates into the interstices of the fibre. Similarly in the fixing bath the tartar emetic penetrates rapidly, thus forming an insoluble antimony compound. In the Methylene Blue bath the dyestuff, being again highly dispersed, penetrates to form a complex lake tannin-antimony-Methylene Blue, and the fastness of the dyeings will depend on the insolubility of this lake.

MERCERISING.

Measurement of the strength of single fibres of cotton both before and after mercerising showed that this process did not increase the strength of the fibres. This was found to be the case both when the fibres were allowed to shrink during the action of the caustic soda solution and when they were kept stretched. This observation is of importance in showing that the increase in strength of cotton yarn during mercerising is due to a physical change in the association of the fibres. Further investigation in this direction is required and also as regards the theory of the increase in lustre due to mercerisation. For instance, W. Harrison [72] inclines to Lange's view that lustre is due to the smoothness of the surface of the mercerised fibres as compared with the ordinary cotton fibres. He maintains that the lustre of single fibres is decreased by increasing the number of twists.[73]

PRINTING.

In the fixation of acid mordant dyestuffs, e.g. alizarin, in calico-printing the formation of the colour-lake is stated to be due [74] to

[71] *Kolloid Zeits.*, 1918, **23**, 100 ; *J.*, 1918, **729A**.
[72] *Second Brit. Ass. Report on Colloid Chemistry*
[73] Compare *Annual Reports*, 1918.
[74] H. Pomeranz, *Monatsschr. Text. Ind.*, 1918, **33**, 30, 38, 45 ; *J.* 1919, **39A.**

reactions between the fibre, mordant, and dyestuff leading to the production of a colloidal colouring matter, which also reacts with the colloidal alumina deposited on the fibre. The oil employed exists both as a constituent of the colour lake and in direct combination with the cotton. R. Haller [75] states that zinc and manganese salts act as a reserve in Indanthrene dye-baths. If a vat dyestuff be added to such a reserve together with stannous oxide and anthraquinone, it is possible, by simply dipping the printed goods into an Indanthrene dye-bath, to fix the colour; the alkali of the dye-bath penetrates the reserve and, in conjunction with the stannous oxide, reduces the vat dyestuff, while the zinc and manganese salts prevent the reserve from taking up the colour of the dye-bath. Still better results are obtained if " Hydro-sulphite conc." and a solution of potassium sulphate are added to the printing colour. H. Pomeranz [76] states that it is still unexplained how the neutralisation of the alkali and its action as a fixing agent can proceed simultaneously. He explains the action as being due to the different properties of the dyestuffs used, pointing to the possibility of the unreduced easily-vatted dyestuff acting as an oxidising agent on the more difficultly vatted dyestuff and so acting as a reserve. But Haller [77] contends that the hydroxides of zinc and manganese are in a colloidal form presenting a membrane impenetrable by the Indanthrene, which is in a colloidal form in the dye-vat but penetrable by the caustic soda of the vat.

Insoluble gums are converted into soluble form by treating with sodium or potassium peroxide, percarbonate, persulphate, or per-silicate. They can be bleached if necessary with hypochlorites and are then suitable for use as thickeners in calico printing.[78] Coloured dis-charge effects are produced on cotton by printing a sulphur or vat dyestuff with a suitable reducing agent on, or under, a metallic mor-dant together with sodium citrate, tartrate, or lactate. The citrate discharges the mordant in the printed parts when the goods are steamed and finally dyed with a mordant dyestuff [79]

FINISHING

The mechanical treatments to which fabrics are subjected during finishing are mainly mechanical pressure, heat and moisture.[80] The effect of moisture is to increase the swelling of the fibre, and this is greater the higher the temperature. Pressure increases the swelling

[75] Färber-Zeit., 1917, **28**, 247 ; J., 1918, 462A.

[76] Färber-Zeit., 1917, **28**, 369 ; 1918, **29**, 5, 51 ; J., 1918, 462A, 688A.

[77] Färber-Zeit., 1918, **29**, 1 ; J., 1918, 688A.

[78] The Calico Printers' Assoc., Ltd., J. B. Fothergill, and G. W. Wilson, Eng Pat. 120183 ; J., 1919, 10A.

[79] The Calico Printers' Assoc., Ltd., F. Ashton, and G. Nelson, Eng. Pat. 120512 ; J., 1919, 10A.

[80] W. Harrison, Second Brit. Assoc. Report on Colloid Chemistry.

in the direction in which it is applied. Permanent finishes are produced by processes which reduce the swelling capacity of the fibre colloids. It has been found [81] that there is an appreciable loss in the strength of woollen fabrics during crabbing, scouring, and " permanent " finishing. " Crimps " is a source of trouble and is sometimes caused by irregular artificial conditioning.

On treating cotton with caustic soda of less than mercerising strength and then submitting it to the action of carbon bisulphide, a hydrated derivative is produced which is not soluble in water.[82]

The changes undergone by starch during boiling are of importance to many industries, particularly to finishing, and the effect of the addition of salts on these changes is of interest to those preparing compound starch mixings.[83] Glue has again [84] been recommended as a substitute for starch, and along with mucilages from various seeds for the finishing of curtains and embroidery.[85] The glue should be properly decolorised before use in order to avoid marking. Starch substitutes were in great demand during the war, but now, with conditions more normal, these substitutes are not of such vital importance. By extracting seaweed with water and treating the extract with formaldehyde a material suitable for finishing is said to be obtained.[81]

The methods of waterproofing cloth have recently been discussed,[87] and tests described for determining the efficiency of the proofing. Basic aluminium acetate or formate has been suggested for use previous to wax-proofing lightly woven fabrics.[88] A process of rendering fabrics less inflammable by first treating them with sodium aluminate and then with carbon dioxide under pressure and at a high temperature has been protected.[89] Fabrics are said to be rendered invisible by padding them with an aluminium salt, adding colouring matters which are fixed by the aluminium salt, fixing the colour by ageing, and then running through a wax solution.[90] It has been found that zirconium sulphate cannot be used in place of tin salts for the weighting of silk.[91]

[81] E. Midgley, *J. Soc. Dyers and Col.*, 1919, **35**, 20 ; 1919, 102A.
[82] C. F. Cross and E. J. Bevan, Eng. Pat. 126174 ; *J.*, 1919, 458A.
[83] Samec, *Kolloidchem. Beihefte*, 1916, 33.
[84] See *Annual Reports*, 1918.
[85] A. Winter, *Färber-Zeit.*, 1919, **30**, 104 ; *J.*, 1919, 626A.
[86] W. H. Hyatt and E. N. Fellowes, Eng. Pat. 131443 ; *J.*, 1919, 761A.
[87] G. Martin and J. Wood, *J.*, 1919, 84T.
[88] E. Jentzsch, *Färber-Zeit.*, 1918, **29**, 3 ; *J.*, 1918, 688A.
[89] P. Spence & Sons, and T. J. I. Craig, Eng. Pat. 130461 ; *J.*, 1919, 716A.
[90] F. Cochrane, Eng. Pats. 129712 and 130672 ; *J.*, 1919, 760A.
[91] E. Ristenpart, *Färber-Zeit.*, 1918, **29**, 26 ; *J.*, 1918, 687A.

ACIDS, ALKALIS, SALTS, ETC.

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The year under review is the first year of comparative peace following four years of uninterrupted war. The literature of the period is, therefore, naturally concerned almost exclusively with work done during the war, much of which could not be published before the termination of hostilities. The manufacture of sulphuric and nitric acids and of ammonium nitrate needed for making explosives, and the search for new sources of potassium salts to replace the vanished German supplies are especially prominent in the literature dealt with in this section. The realisation of the supreme importance of a secure supply of nitric acid in time of war has forced all the belligerent nations to devote very special attention to methods of fixing atmospheric nitrogen, to the recovery of ammonia from the distillation of coal, and to the steps leading from primary products like cyanamide or ammonia to nitric acid. Much of this work is of permanent value, since nitrogenous fertilisers will do much to repair the ravages caused by the warlike use. of nitric acid. The same cannot be said of the processes and plants intended for the manufacture of many other substances which have a limited, or no utility for peaceful purposes.

The problems of reconstruction occupy as yet a comparatively small place in the literature. It seems certain, however, that the great increase in cost of the basic raw material, coal (average price at the pit-head 10s. 1$\frac{1}{2}d$. per ton in Great Britain in 1913, 29s. in July, 1919), and in the cost of labour will displace manufacturing equilibrium in the direction of those methods which make the most economical use of both of them. The high cost of transportation may also produce geographical re-groupings.

It is to be hoped that the proposals to publish compendia of chemistry [1] and to establish an interallied system of abstracts [2] may soon materialise. They would add materially to the efficiency of the chemist's work.

[1] W. P. Wynne, *J.*, 1919, 239a ; *J. Ind. Eng Chem.*, 1919, 11, 415.
[2] Sir W. Pope, *J.*, 1919, 208t

NITROGEN COMPOUNDS.

During the war the world's production of fixed nitrogen has continued to increase, at about the same rate as before. The following table is compiled from the statistics which have appeared during the past year, some of which, however, only profess to be approximations. Complete figures are not available for 1918.

World's Production in 1000 tons Nitrogen.

	Chile nitrate	Ammonia from coal.	Cyanamide.	Nitric acid (arc process)	Ammonia (Haber)	Total.
1909 . . .	298	207	20	5	0	530
1913 . . .	382	308	31	20	4	745
1917 . . .	382	432	115	34	101	ʿ1094
1918 . . .	‑	—	169	—	160	—

German Production in 1000 tons Nitrogen.

1909 . . .	101*	72	2	0	0	175
1913 . . .	120 *	97	5	0	4	226
1917 . . .	0	140	80	0	101	321
1918 . . .	0	‑‑	60	0 .	160	‑‑‑

* Consumption.

Before 1914 the annual increase in the production of fixed nitrogen was absorbed by agriculture ; since then a large part of the supply has been diverted to the manufacture of explosives and agriculture has had to go short. To make up for the cessation of imports of sodium nitrate Germany, after the battle of the Marne in the spring of 1915, began to develop the cyanamide process, which was then the best known method of fixing nitrogen. The Berlin-Anhaltische Maschinenbau Akt.-Ges. is reported to have erected thirty plants with a monthly capacity of 100,000 tons of nitric acid [4] ; three Government plants were also started, and the Badische company received a subsidy of 30 million marks for the extension of the Haber plant. After the entry of the United States into the war a somewhat similar development occurred there. Government plant No. 1, working the General Electric Co.'s process for synthesising ammonia from its elements, came into operation in September 1918, and plant No. 2, for the cyanamide process, started in November, but neither was worked to its full capacity.[5]

[3] *Chief Inspector of Alkali Works, 55th Report*, 1918 ; *J.*, 1919, 316R.   A. H. White, *J. Ind. Eng. Chem.*, 1919, 11, 234.   *Dept. Committee on Sulphuric Acid, etc.*; *J.*, 1919, 90R.   R. E. McConnell, *J. Ind. Eng. Chem.*, 1919, 11, 837 ; *J.*, 1919, 351R ; *J.*, 1919, 378R.   Internat. Inst. Agric., May, 1919, *J.*, 1919, 271R.
[4] *Z. angew. Chem.*, Mar., 1919 ; *J.*, 1919, 189R.
[5] A. H. White, *J. Ind. Eng. Chem.*, 1919, 11, 231.

Ammonia.

A striking feature of the statistics quoted above is the rapid development of the Haber process. Production of ammonia by this process began in 1913 at the Oppau works; in April 1917 a new works at Leuna, near Merseburg, was started.[6] R. E. McConnell[7] reports the output of the Oppau works as 90,000 tons of nitrogen for the year ending November 1 1918; the Leuna works is fixing 200 tons of nitrogen daily, and extensions are in progress which will increase this to 560 tons.[8] Owing to the low cost, estimated by McConnell at 5½d. per lb. of nitrogen, which includes the cost of converting a large part of the ammonia into nitric acid, these works are expected to be permanent producers.

The direct synthesis of ammonia is under investigation in the allied countries, although comparatively little has been published on the subject. G. Claude[8] proposes to use the mixture of hydrogen and nitrogen at pressures exceeding 500 and even 2000 atmospheres. The patents of E. B. Maxted[9] and of R. C. Parsons[10] for the removal of traces of carbon monoxide and for the preparation of pure hydrogen respectively are of interest as indicating the great precautions necessary to obtain sufficiently pure gases in this process.

E. B. Maxted[11] has continued his work on the synthesis of ammonia from hydrogen and nitrogen at high temperatures. Over 1% of ammonia can be obtained by the passage of the $N_2 + 3H_2$ mixture through a high-tension arc at atmospheric pressure — a result otherwise obtainable only at a temperature of about 350° C. This result confirms Maxted's view that the equilibrium quantity of ammonia passes through a minimum at some intermediate temperature. E. Briner and A. Baerfuss[12] have made similar observations.

Ammonium Salts.

The enormous quantities of high explosives required for shell-filling (220,000 tons in 1917 in Great Britain alone) could not be made from the available supplies of phenol and toluene. This difficulty was surmounted by the use of amatol, a mixture of trinitrotoluene with two to four times its weight of ammonium nitrate, which involved an increase in the output of the latter from about 100 tons to 3000 tons

[6] J., 1919, 378R.

[7] J. Ind. Eng. Chem., 1919, 11, 837 ; J., 1919, 351R.

[8] L'Air Liquide, Soc. Anon. pour l'Etude des proc. G. Claude, Eng. Pats. 130086 and 130087, 1918 ; J., 1919, 718A.

[9] Eng. Pat. 131049, 1918 ; J., 1919, 718A

[10] Eng. Pat. 130069, 1918 , J., 1919, 680A.

[11] Chem. Soc. Trans., 1919, 115, 113 ; J., 1919, 219A.

[12] Helv. Chim. Acta, 1919, 2, 95 ; J., 1919, 219A. J. Chim. Phys , 1919, 17, 71 ; J., 1919, 572A.

weekly.[13] Details of the methods of manufacture employed have appeared recently.

D. Tyrer [14] and F. A. Freeth and H. E. Cocksedge [15] set out from sodium nitrate and ammonium sulphate ; a hot concentrated solution is made from which the greater part of the sulphate separates as the anhydrous sodium salt. The filtrate is cooled and diluted somewhat. In Freeth and Cocksedge's method the dilution is sufficient to prevent the separation of sodium salts so that on further cooling pure ammonium nitrate is deposited. According to Tyrer 60% of the remaining sulphate is precipitated with calcium nitrate and the filtrate further concentrated to obtain ammonium nitrate. In both cases the residual mother liquor returns to the process.

Calcium nitrate is prepared [16] from calcium chloride and sodium nitrate, sodium chloride separating at 80° and calcium nitrate tetra-hydrate crystallising from the filtrate below 30° C.

A modification of the ammonia-soda process using sodium nitrate in place of the chloride [17] was also used.

W. T. Gidden [18] describes an ingenious process in which nitric acid and ammonia gas are fed into a pan and the slightly alkaline product maintained at 145°-155° C. by adding water as required. The heat of reaction is sufficient to evaporate all the water, leaving dry, fused ammonium nitrate. E. B. R. Prideaux and R. M. Caven [19] have determined the vapour pressures of ammonium nitrate solutions and calculated the heat of evaporation of water from them. Owing to slight hydrolysis the solutions attack iron vessels, a loss of ammonia and a product contaminated with iron resulting. Glass or aluminium vessels are unacted on.

A good deal of interest has been shown in the preparation of a dry, neutral ammonium sulphate, five patents having been granted for different ways of adding the necessary ammonia.[20]

H. M. Dawson, continuing his work, referred to last year, on the system $Na_2SO_4, (NH_4)_2SO_4, H_2O$, [21] shows that $(NH_4)_2SO_4 . Na_2SO_4 . 4 H_2O$ crystallises from suitable solutions at all temperatures between 59·3° and − 16° C. Setting out from nitre cake with 30% free acid, for example, a neutral solution containing 15% of Na_2SO_4

[13] H. Louis, J., 1919, 201T.

[14] Eng. Pat. 125621, 1916; J., 1919, 414A.

[15] Eng. Pat. 126678, 1917; J., 1919, 499A. Also A. C. D. Rivett, Eng. Pat. 131358, 1918; J., 1919, 764A.

[16] J. G. Gilbert, Eng. Pat. 124780, 1916; J., 1919, 323A.

[17] Freeth and Cocksedge, Eng. Pat. 12410, 1915; J., 1919, 253A.

[18] Eng. Pat. 6048, 1915; J., 1919, 253A.

[19] J., 1919, 353T.

[20] Eng. Pats. 121082, 127398, 127715, 127716, 129850, 1918; J., 1919, 74A, 499A, 536A, 680A.

[21] Annual Reports, 1918, 168.

and 35% of $(NH_4)_2SO_4$ is prepared by adding ammonia and sulphuric acid ; on cooling this from 60° to 15° C. the double salt is obtained and the mother liquor can be re-used . 62% of the sulphuric acid is obtained from the nitre cake.[22]

J. W. Cobb's process for making ammonium sulphate without the use of sulphuric acid is described in the Alkali Works Report for 1918.[23] Coal gas is scrubbed through a solution of zinc sulphate, the zinc sulphide, produced from the hydrogen sulphide accompanying the ammonia, is roasted to zinc oxide and sulphur dioxide, and zinc sulphate solution regenerated by passing the latter, mixed with air, through a suspension of the zinc oxide

Calcium Cyanamide.

A. J. Allmand and E. R. Williams[24] describe the plant used by the A.-G. fur Stickstoffdunger at Knapsack, near Cologne, for the conversion of powdered calcium carbide into cyanamide. This consists of a horizontal iron tube, 150 ft. × 6 ft., encased in brickwork for half its length ; twenty-eight trucks each carrying fourteen boxes (30 × 20 × 13 in.) full of carbide are pushed into the tube, the end doors closed, and the temperature of the charge raised by direct contact with gas flames. The gas and air supply is then stopped and nitrogen turned on. A charge requires 28 hours and only a superficial crust of lime is formed, the bulk of the product containing 20% of nitrogen.

A somewhat similar process is patented by G. E. Cox,[25] whilst O. F. S. Carlson[26] proposes to treat the carbide, mixed with calcium chloride or fluoride, with nitrogen in a multi-stage furnace with stirrers on each shelf.

Cyanides

A quantity of low-grade cyanide has been manufactured by fusing calcium cyanamide with salt, using the methods patented by H. Freeman[27] and H. P. Eastman.[28]

An interesting account is given by C. O. Brown[29] of the plant erected by the U.S. Government at Saltville, to work the Bucher process for making cyanide by the action of nitrogen on a mixture of sodium carbonate and carbon in presence of iron The plant was completed only a few days before the termination of hostilities, and after a short run was shut down. The cyanisation process was carried out in

[22] J., 1919, 98T.
[23] Chief Inspector of Alkali Works, 55th Report ; J., 1919, 378R.
[24] J., 1919, 304R.
[25] U.S. Pat. 1282395 ; J., 1919, 12A.
[26] Eng. Pat. 123796, 1918 ; J., 1919, 253A.
[27] U.S. Pat. 1282405 ; J., 1919, 41A.
[28] U.S. Pat. 1282395 ; J., 1919, 12A.
[29] J. Ind. Eng. Chem., 1919, 11, 1010.

externally heated iron tubes at 1000° C. The product was leached with liquid, anhydrous ammonia ; this dissolves practically nothing but sodium cyanide. By careful attention to the design of the lixiviating and evaporating plant the loss of ammonia was kept down to 2% of the weight of cyanide made,[30] the product containing 92% NaCN.

NITRIC ACID.

The large quantities of nitric acid required in 1918 were made in the allied countries mostly from sodium nitrate, although appreciable quantities were also made by the oxidation of ammonia.[31] In Germany the latter process was used practically exclusively ; sodium nitrate was, however, made in large quantities from the oxides of nitrogen. The Badische Co., for example, turned out nearly one-third of the nitrogen fixed at Oppau in this form [32] in 1918, and a similar procedure was followed at Leverkusen.[33]

The use of nitrous gases, made from ammonia in sulphuric acid chambers, was extended and continued to give satisfaction.[31]

The quantities of material used in making nitric acid and the working costs in the Government factories are given in the Second Report of the Department of Explosives Supply.[34] In nine factories from 1·423 to 1·496 tons of sodium nitrate and from 1·348 to 1·820 tons of sulphuric acid were used per ton of 100% nitric acid produced. Working costs varied from £3·728 to £11·643 per ton.

Interesting descriptions of the methods employed in the catalytic oxidation of ammonia have been published by W. S. Landis [35] and C. L. Parsons.[36] The original Ostwald process was installed early in the war both in France and England, but was not used in Germany. Its characteristic features are the use of an ammonia-air mixture preheated to about 600° C. by heat exchange with the outflowing gases, and the use of a cylinder of platinum foil as catalyst. The units are small, and some decomposition of ammonia occurs in contact with the nickel preheating surface.

The process used in Germany was developed immediately after the outbreak of war in 1914. It was a development of Kaiser's process in which the cold mixture of air and ammonia passed through an electrically heated platinum gauze stretched across the tube carrying the gases. In 1916 electrical heating was found to be unnecessary, the process being thermally self-sustaining if multiple gauzes are used and

[30] U.S. Pats. 1313313, 1314236, and 1314237 ; J., 1919, 765A.
[31] Inspector of Alkali Works Rep., 1918 ; J., 1919, 317R.
[32] R. E. McConnell, J. Ind. Eng. Chem., 1919, 11, 837 ; J., 1919, 351R.
[33] Allmand and Williams ; J., 1919, 285R.
[34] J., 1919, 224R.
[35] Chem. and Met. Eng., 1919, 20, 470 ; J., 1919, 410A.
[36] J. Ind. Eng. Chem., 1919, 11, 541 ; J., 1919, 497A.

the gases made to flow downwards. The electrically heated gauze was used in the United States plant at Muscle Shoals; each unit has a capacity of 0·35 ton of 100% HNO_3 per day; 5½ to 6 lb. of ammonia is oxidised per sq. ft. of gauze per hour with an efficiency of 90%. The electrical energy required is 1·7 kilowatt hour per lb. of nitric acid.

In the apparatus described by Parsons, electrical heating is unnecessary, the gauze and surrounding brickwork being so arranged that the heat of reaction is conserved.[27] Platinum gauze (80-mesh, 0·0026 in. wire) is rolled into a cylinder 9 m dia and 13 in. long, having a quadruple layer of gauze; the cylinder is suspended in a brick casing so that the gases enter at its upper end and pass through it, the lower end being closed by a quartz plate. Working conditions are: 200 cub. ft. per minute of gas containing 10–11% of ammonia, yield 2½ tons of nitric acid per day, efficiency being about 92%. The working temperature of the gauze is 825 C. The hot ammonia-air mixture comes in contact with nothing but quartz, nickel, or aluminium before reaching the catalyst.

Platinum and palladium are much the best catalysts for the reaction, but palladium gauze falls to powder after a few hours. The addition of 1% of iridium to the platinum strengthens the gauze considerably; details of construction from the gauze-makers' point of view are given by A. A. Campbell.[38] Some non-metallic catalysts give good efficiency, but require much larger quantities of material and larger apparatus than platinum.

Traces of iron in the platinum or introduced with the gases are to be avoided; as little as 0·2% affects the efficiency. G. B. Taylor and J. H. Capps[39] find that phosphine is extraordinarily poisonous, 2 or 3 parts in 100 million of the ammonia-air mixture reducing the efficiency of the platinum catalyst several per cent. The apparently poisonous action of acetylene noticed in last year's Report (p. 171) is traced to this source, pure acetylene being harmless; the same appears to be true of small quantities of hydrogen sulphide.

A smooth surface of platinum has very little catalytic activity; a new gauze must, therefore, be "activated" by heating it for some hours (most conveniently by an electric current) in a rather rich mixture: the active surface is grey and spongy. Organic substances which leave a permanent deposit on the platinum act as poisons, but hydrocyanic acid is as easily oxidised to nitric acid as ammonia itself.

A. J. Allmand and E. R. Williams[40] give details of a German plant using iron oxide as catalyst; a direct comparison of its dimensions with that of a platinum unit is impossible since the output is not given.

[27] L. C. Jones and C. L. Parsons, Eng. Pat. 132551, 1918; J., 1919, 817A.
[38] J. Ind. Eng. Chem., 1919, 11, 468; J., 1919, 410A.
[39] J. Ind. Eng. Chem., 1919, 11, 27; J., 1919, 132A.
[40] J., 1919, 285R.

The gas, containing 7–10% NH_3, is preheated to 250° C. and passed over granular iron oxide containing " some heavy metal oxide " spread in 4–5 in. layers on perforated tiles in a tower 14 ft. dia. and 18 ft. high and kept at 700°–800° C.   The efficiency is 80–85%.

Other catalysts proposed are a mixture of iron and copper oxides with lime [41] and chromium oxide.[42]

Conversion of Nitric Oxide into Nitric Acid.

P. Jolibois and A. Sanfourche [43] support the old view that nitric oxide is oxidised by oxygen to N_2O_3 very rapidly, further change to NO_2 occurring much more slowly, and in presence of water not at all. The reaction $2HNO_3 + N_2O_3 = 2N_2O_4 + H_2O$ begins in acid of 50% strength and becomes more important as the strength increases, so that no more than 68% strength is attainable.

J. Knox and D. M. Reid [44] show that the rate of decomposition of aqueous nitrous acid is enormously affected by supersaturation with nitric oxide. For example, shaking a $N/20$ solution increases the decomposition from 5·8% in one hour to 91·5%.

The design of towers for absorbing nitric oxide is discussed by J. R. Partington and L. H. Parker.[45] When the acid entering and leaving the tower is about the same strength the behaviour of the tower is given by

$$\log_e \frac{c_o}{c_x} = \frac{Kkv}{V},$$

where c_o and c_x = lb. NO_2 per cub. ft. of gas entering and leaving the tower respectively, K is a " coefficient of absorption " obtained by trial, k = sq. ft. of absorbing surface per cub. ft. of tower space, v = gross volume of tower, and V the flow of gas in cub. ft. per minute. The numerical values of K and k are tabulated so that the dimensions of a tower required for any duty can be calculated.

Nitrates.

Interesting details of the cost of production of Chile saltpetre are given by J. Marco [46]; the methods employed are said to be often primitive. At four plants the cost of mining and extraction (55–72% of the $NaNO_3$ is extracted) varies from 13·4 to 20·6 dollars (U.S.A.) per 2000 lb. of 95% $NaNO_3$. The cost of putting on board ship is about 18 dollars (65% of which is Government tax).

[41] E. B. Maxted and G. R. Ridsdale, Eng. Pat. 10781, 1915 ; J., 1919, 252A.

[42] H. E. F. Goold-Adams, J. R. Partington, and E. K. Rideal, Eng. Pat. 126716, 1917 ; J., 1919, 499A.

[43] Comptes rend., 1919, 168, 235 ; J., 1919, 132A.   A. Sanfourche, Comptes rend., 1919, 168, 307, 401 ; J., 1919, 172A, 219A.

[44] J., 1919, 105T.   [45] J., 1919, 75T.

[46] J. Ind. Eng. Chem., 1919, 11, 780 ; J., 1919, 351R.

The existence of potassium nitrate in shales covering some hundreds of square miles north of the Orange River in South Africa has been known for some time. According to E. G. Bryant[47] the shales vary in thickness from 10 to 30 ft., and carry as much as 25% of KNO_3; a company has been formed to work them.

SULPHURIC ACID

The pre-war consumption of sulphuric acid in the United Kingdom was 956,000 tons (100% acid) per annum[48] The productive capacity (tons 100% acid) is:—

	Pre war	Present time
Oleum	22,000	450,000
Chamber	1,040,000	1,265,000
	1,062,000	1,715,000

Before the war the superphosphate and ammonium sulphate industries were the largest consumers (taking 300,000 and 280,000 tons respectively). During the war of course the output was mostly used for explosives. The German production in 1912 was 1,650,000 tons (100%), made mostly from imported pyrites and zinc blende. At present kieserite and gypsum are said to be used, Germany being independent of foreign supplies.[49] Switzerland has also developed the use of gypsum.[50]

The increased quantities of oleum noted above have been made in Grillo, Mannheim, and Tentelew plants; details of their performance are given in the Second Report of the Department of Explosives Supply.[51] R. Curtis[52] contributes an account of the Grillo process. A unit making 25–30 tons of SO_3 per day consists of two converters in parallel, each containing 10,000 lb. of calcined magnesium sulphate impregnated with 0·3% of platinum. The mass is distributed on four trays. The entering gases (from sulphur) are preheated, by exchange with the outgoing gases, to 350° C., and the trays are maintained at 380°, 470°, 460°, and 440° C. The conversion is 96–97%. Purification of the entering gases is effected by filtration through coke at a slow rate and drying with strong sulphuric acid. Curtis concludes that for ores yielding very impure gas the chamber process is cheaper, but in all other cases the contact process is to be preferred.

S. T. T. Geary[53] and R. Curtis[54] give some data on the effect of temperature of the contact mass on its efficiency.

Goldmann[55] states that the platinum used for converting gases with

[47] J., 1919, 360т.
[48] Rep. Dept. Committee on Sulphuric Acid and Fertiliser Trades, 1919; J.,1919, 90з.
[49] J., 1919, 352з.   [50] J., 1919, 113з.   [51] J., 1919, 225з.
[52] J., 1919, 360з.   [53] J., 1919, 133т.   [54] J., 1919, 196т.
[55] Metall und Erz, 1919, 16, 41, J., 1919, 251а.

4-5% SO_2 made from galena worked for three years without renewal.

Patents have been granted for the use of electrical precipitation for purifying burner gases [56] and for recovering valuable constituents from fumes escaping from sulphuric acid plant.[57]   Welch [58] also proposes to make use of the reaction $SO_2 + 2H_2O + Cl_2 = H_2SO_4 + 2HCl$, the sulphuric acid mist being separated from the hydrochloric acid by electrical precipitation.

An interesting account of F. G. Cottrell's pioneer work on electrical precipitation was given on the occasion of the presentation to him of the Perkin Medal.[59]

The Chief Inspector of Alkali Works reports [60] that plants working with limited chamber capacity continued to give satisfaction during 1918. Combinations of these with the older type are criticised on the ground that the larger concentration of nitrous gases required for the shorter time of reaction in the small chambers is unsuited to the conditions in the large chambers and *vice versâ*. K. B. Quinan [61] patents a system in which the reaction between sulphur dioxide and nitrous gases and that between gas and liquid take place in separate chambers ; the gas-liquid reaction is brought about by distributing the liquid over a permeable diaphragm through which the gases pass, percolation of the liquid being largely prevented.

The manufacture of sulphuric acid from calcium sulphate (waste from sulphonations) at Leverkusen, near Cologne,[62] is carried on by the cement process, the sulphur dioxide evolved being converted into the trioxide by a contact process. Considerable difficulties have been encountered which are not yet overcome.

The substitution of gypsum for sulphuric acid in making ammonium sulphate has apparently been tried in Germany,[63] ammonia, calcium sulphate, and carbon dioxide being brought together.

The removal of arsenic from sulphuric acid is the subject of a patented process in which the precipitate of arsenic sulphide formed at 71° C. is collected together as a scum by shaking the acid with $\frac{1}{2}$-$2\frac{1}{2}$ gallons of paraffin oil per ton of acid. After removing the scum it is treated with alkali, which yields a solution of sulpharsenite and a layer of oil, which can be re-used.[64]

Cases in which cast-iron blowers which had been used for mixtures of sulphuric and nitric acids suddenly disrupted into small fragments

[56] H. V. Welch, U.S. Pat. 1284167 ; *J.*, 1919, 74A.   L. Bradley, U.S. Pats. 1284175-6 ; *J.*, 1919, 74A.
[57] H. V. Welch, U.S. Pat. 1284166 ; *J.*, 1919, 73A.
[58] H. V. Welch. U.S. Pat. 1285856 ; *J.*, 1919, 133A,
[59] *J.*, 1919, 121T.   [60] *J.*, 1919, 317R.
[61] Eng. Pat. 130712, 1918 ; *J.*, 1919, 717A.   [62] *J.*, 1919, 285R.
[63] *J.*, 1919, 378R.
[64] A. E. Wareing, and United Alkali Co., Eng. Pat. 126714, 1917 ; *J.*, 1919, 461A.

are described by A. C. Cumming,[64] who attributes the occurrence to the penetration of the porous metal by acid and consequent growth of crystals in the interior of the metal.

Nitre Cake

The equilibria in the system $Na_2SO_4 - H_2SO_4 - H_2O$ have been studied by P. Pascal and Ero,[66] H. M. Dawson,[67] and H. W. Foote.[68] The salts which can exist are Na_2SO_4, and its hepta- and deca-hydrates; $Na_2SO_4.NaHSO_4$; $NaHSO_4$; $NaHSO_4.H_2O$; $NaHSO_4.H_2SO_4$; $NaHSO_4.H_2SO_4.1\frac{1}{2}H_2O$. $2NaHSO_4.Na_2SO_4$. The whole of the sulphuric acid can be recovered in the form of a solution containing 27% H_2SO_4 and 2·8% Na_2SO_4 by cooling a solution of the acid sulphate (sp. gr. 1·315) to $-20°$ C, when Glauber salt crystallises out.

Foote has also studied the effect of adding copper sulphate to the system. The sparingly soluble salt $Na_2SO_4.CuSO_4.2H_2O$ separates out under a wide range of conditions. Difficulties in pickling copper with nitre-cake solutions may be due to the formation of a film of this salt.

Sulphuryl Chloride

The combination of sulphur dioxide and chlorine in presence of charcoal is patented by W. J. Pope,[69] and in presence of terpenes or certain esters by A. Boake, Roberts, & Co., and T. H. Durrans.[70]

POTASSIUM SALTS.

The search for sources of potassium salts to take the place of the German supply again occupies a prominent place in the literature. Material progress has been made, although, now that the Alsace deposits are becoming available and some importation from Germany is permitted,[71] the situation is less critical.

In the United States the potash industry began in 1914; in 1917 the output reached 32,366 tons of K_2O, which increased in 1918 to 52,135 tons,[72] obtained from the following sources. Natural brines (Nebraska),[73] 39,255 tons K_2O, alunite, 2619; cement kiln dust, 1429; kelp, 4292; molasses distillery waste, 3322; beet sugar, strontia process, 761; wood ashes and other sources, 457. The pre-war consumption was about 261,000 tons K_2O annually, but it is suggested that this

[64] J., 1919, 31T.
[66] Bull. Soc. Chim., 1919, 25, 35; J., 1919, 220A.
[67] Eng. Pat. 127677, 1917; J., 1919, 535A.
[68] J. Ind. Eng. Chem., 1919, 11, 629; J., 1919, 573A.
[69] Eng. Pat. 122516, 1918; J., 1919, 175A.
[70] Eng. Pat. 124542, 1918; J., 1919, 361A.
[71] J., 1919, 338R.
[72] Bd. of Trade J., Sept. 25, 1919; J., 1919, 374R.
[73] J. M. Lliteras, Chem. and Met. Eng., 1918, 19, 633; J., 1919, 39A.

was unnecessarily large owing to the propaganda of the Kalisyndicat.

The natural brines contain the sulphates and carbonates of sodium and potassium with smaller quantities of chloride. After preliminary concentration by solar heat, they are evaporated to saturation in multiple-effect evaporators and then dried in rotary kilns.

Alunite, a basic sulphate of potassium and aluminium, is calcined, which converts it into a mixture of alumina and potassium sulphate, from which the latter is extracted with water. The numerous processes devised for extracting potash from silicates have not yet borne fruit.[71]

Kelp.

Two methods of treatment of kelp have been used. The more usual of the two is to dry the kelp and then distil it to obtain oils, creosote, ammonia, and pitch. The charred residue is extracted with water, high grade potassium chloride being obtained from the solutions by fractional crystallisation, with iodine as by-product. The residual charcoal, after extraction with hydrochloric acid, is a very active decolorising carbon. A full account of these operations as carried out at the experimental plant of the U.S. Dept. of Agriculture in California is given by J. W. Turrentine and P. S. Shoaff.[75] The industry does not pay if potassium salts are the only products obtained. The second method was developed by the Hercules Powder Co. at San Diego, California ; it depends on the fermentation of the kelp yielding acetone and other products in addition to potassium salts. This process also only pays under war conditions.[76]

Cement Kiln Dust.

Fifteen plants are collecting (or preparing to collect) potash from this source in the United States ; very little has been done in Great Britain. A. W. G. Wilson [77] describes the methods used. The kiln charge contains from 0·5 to 1·04% K_2O, the dust collected carries from 8 to 28 lb. of potash salts per ton of charge, mainly in the form of sulphate. The addition of salt to the charge increases the quantity of potash which can be recovered. The hot gases leaving the kilns are treated either by water sprays or by electrical precipitation.

In the first method the spray is applied to the gas in flues of large cross-section, in order to have a slow current of gas ; the solution obtained is filtered from insoluble dust and re-circulated until it contains about 3½% of potash salts, when it is evaporated. Stronger solutions deposit the salts in the flues owing to the considerable evaporation which takes place. The Cottrell precipitators are worked either dry or wet. In the former case duplicate sets of tubes are provided, the dust

[74] U.S. Geol. Survey, Mar., 1919; *J.*, 1919, 248R.
[75] *J. Ind. Eng. Chem.*, 1919, **11**, 864.
[76] C. J. Berkeley, *J.*, 1919, 202R.   [77] *J.*, 1919, 314T.

being shaken down from the one set while the gases are passing through the other. In the wet systems the walls of the tubes are constantly washed by a film of water which carries the dust away as fast as it is deposited. In either case the dust is extracted with water at about 85° C.

When the dust contains calcium sulphate as well as potassium sulphate the sparingly soluble double salts, $K_2SO_4.CaSO_4.H_2O$ (syngenite) and $K_2SO_4.5CaSO_4.H_2O$, may be formed. E. Anderson[78] shows, however, that owing to their slow rate of formation, a lixiviation loss due to this cause is easily avoided

A variable part of the potash contained in the dust is insoluble even in acids. A. R. Merz and W. H. Ross[79] bring forward evidence to show that part of the potash vaporised in the hottest zone of the kiln combines with the siliceous ash of the coal, used in firing, to form compounds resembling glass. In an oil-fired kiln 91·6% of the potash was soluble, whilst in three coal-fired kilns the soluble portion varied from 19·6 to 59·6%.

Several patents deal with methods of rendering the potash more soluble by preliminary heating of the dust[80] (heating the insoluble silicates with lime has this effect[79]), by treating the dust with solutions of sodium nitrate or chloride,[81] or by leaching at temperatures above 100° C.[82]

The nearly related recovery of potash from blast furnaces is the subject of an important paper by E. C. Rossiter and C. S. Dingley.[83] A very detailed account of the distribution of potash in the furnace charge and in the slag or gas is given, and the results of adding salt to the charge are described. The authors draw the interesting conclusion that it is possible to obtain the equivalent of 63,000, or perhaps 80,000 tons per annum of potassium chloride from the blast furnaces of Great Britain, a quantity approximately double the pre-war consumption.

Silicates.

Processes continue to be proposed for the recovery of potash from silicates such as felspar : (a) by treating them with calcium compounds at high temperatures[84] ; (b) by digesting them with slaked lime and water[85] ; (c) by treating them with acids such as sulphur, dioxide,[86] hydrogen chloride,[87] sulphuric acid and gypsum.[88]

[78] J. Ind. Eng. Chem., 1919, 11, 327 ; J., 1919, 320A.
[79] J. Ind. Eng. Chem., 1919, 11, 39 ; J., 1919, 178A.
[80] U.S. Pat. 1283261 ; J., 1919, 75A.
[81] U.S. Pats. 1296460, 1296461 ; J., 1919, 362A.
[82] U.S. Pat. 1298154 ; J., 1919, 414A.   [83] J., 1919, 375T.
[84] U.S. Pats. 1285121, 1285122, 1286513, 1289736 ; J., 1919, 105A, 134A, 653A.
[85] U.S. Pat. 1296035 ; J., 1919, 362A.
[86] U.S. Pat. 1286718 ; J., 1919, 134A.
[87] U.S. Pat. 1296141 ; J., 1919, 362A.
[88] U.S. Pat. 1296457 ; J., 1919, 362A.

L

Three patents [89] deal with the separation of sodium and potassium nitrates ; the process depends on the fact that the solubility of the potassium salt diminishes with falling temperature to a much greater extent than that of the sodium salt.

HYDROGEN.

A somewhat novel process for the manufacture of hydrogen is patented by G. Claude. Mixtures of hydrogen and other gases, carbon monoxide for example, are scrubbed with solvents such as alcohol, acetone, or benzene at very high pressures (500 to 2000 atmospheres), [90] or ether at $-60°$ C. may be used with 50 to 300 atmospheres pressure.[91] The hydrogen is the least soluble constituent of the mixtures : the low temperatures required are obtained by expanding the gases liberated from the solvent in a motor, which drives a pump returning the desaturated solvent to the system.[92]

. E. B. Maxted and G. R. Ridsdale [93] use liquid nitrogen to scrub out carbon monoxide, which of course yields a mixture of hydrogen and nitrogen.

A number of modifications of the known methods are also suggested. In the steam-iron process, spathic iron ore is said to retain its activity longer and also to yield purer hydrogen if it is submitted to a preliminary treatment with hydrochloric acid.[94] Spanish and Swedish iron ores do not disintegrate when alternately reduced and oxidised, and they retain their activity for a long time ; Hungarian ores break up, and roasted pyrites is apt to lose activity owing to the formation of a siliceous glaze.[95] For the reduction of the iron oxide, Maxted and Ridsdale recommend the use of water gas containing over 10% of CO_2; deposition of carbon and subsequent formation of carbon monoxide in the steaming process are thus avoided.[96] The rate of reduction is increased by the addition of alkalis or alkaline-earths and copper.[97]

In the process in which water-gas and steam are treated with a catalyst in order to convert the carbon monoxide into dioxide, A. Mittasch[98] uses cerium oxide as catalyst. E. K. Rideal and H. S.

[89] F. A. Freeth and H. E. Cocksedge, Eng. Pat. 124513, 1916 ; *J.*, 1919, 322A. C. W. Bailey, H. S. Denny, and A. T. Jefferis, Eng. Pat. 124960, 1918 ; *J.*, 1919, 322A. G. C. Given and R. H. Barteaux, U.S. Pat. 1294788 ; *J.*, 1919, 323A.

[90] Eng. Pat. 130092, 1918 ; *J.*, 1919, 719A.

[91] Eng. Pat. 130358, 1918 ; *J.*, 1919, 719A.

[92] Eng. Pat. 131091, 1918 ; *J.*, 1919, 765A.

[93] Eng. Pat. 124824, 1916 ; *J.*, 1919, 323A.

[94] Eng. Pat. 122474, 1918 ; *J.*, 1919, 175A.

[95] A. von Skopnik, *Chem.-Zeit.*, 1919, 43, 481 ; *J.*, 1919, 717A.

[96] Eng. Pat. 125112, 1916 ; *J.*, 1919, 364A.

[97] E. B. Maxted, Eng. Pat. 125410, 1916 ; *J.*, 1919, 364A.

[98] U.S. Pat. 1301151 ; *J.*, 1919, 536A

Taylor [99] complete the oxidation of the carbon monoxide by passing the mixture over a second catalyst at a lower temperature. The South Metropolitan Gas Co. and J. M. Somerville [100] treat the gas with a mixture of ferric oxide and caustic soda at temperatures above 400° C.

Pure iridium absorbs up to 140 vols. of hydrogen at 20° C., easily expelled by warming. Platinum black absorbs as much as 160 vols., the maximum occurring at 0° C., but spongy platinum absorbs no more than its own volume of hydrogen. [101]

HELIUM.

The substitution of helium for hydrogen in airships was proposed by Sir William Ramsay in 1915, on account of its non-inflammability ; its lifting power is but little inferior to that of hydrogen, and its rate of diffusion is one-half. A search for sources of the gas led to the discovery that a natural gas at Petrolia in Texas, which was being produced at the rate of 20 million cub. ft. daily, contained 0·9% of helium which can be separated by liquefying all other constituents. A Linde plant started work early in 1918, and a Claude plant a few weeks later ; a third plant, on the new Jefferies and Norton system, was being tried in October 1918. [102] The cost of helium is expected to be 5d. per cub. ft. Another plant is reported at Calgary (Alberta) for separating helium from natural gas. This has a capacity of 15,000 cub. ft. per 24 hrs., at a cost of 1s. per cub. ft. [104]

HALOIDS

Although chlorine has been produced, mostly electrochemically, in enormous quantities during the war—it is required in the production of almost all the lethal substances used—it does not figure prominently in the literature under review. J. Goldschmidt [104] finds that aqueous hypochlorous acid contains small quantities of chlorine monoxide, $2HClO \rightleftharpoons H_2O + Cl_2O$; $N/5$ solutions, for example, contain about 0·02% Cl_2O. By distillation *in vacuo* and condensation at 0°, −20°, and −80° C. respectively, 25% aqueous hypochlorous acid condenses in the first two receivers and pure Cl_2O in the last.

During the war France has developed a supply of bromine, sufficient for domestic consumption, from the salt deposits of Tunisia. [105] Methods of preparing bromine from bittern in the U.S.A., which appear to present no novel features, are described [105] ; the production in 1917 was 450 tons.

[99] Eng. Pat. 129743, 1918 ; *J.*, 1919, 682A.
[100] Eng. Pat. 122781, 1918 ; *J.*, 1919, 175A.
[101] A. Gutbier, B. Ottenstein, and G. L. Weiss, *Ber.*, 1919, 52, 1366 ; *J.*, 1919, 379A. A. Gutbier and O. Maisch, *Ber.*, 1919, 52, 1368 ; *J.*, 1919, 380A.
[102] F. G. Cottrell, *J.*, 1919, 123T.   [103] *J.*, 1919, 268B.
[104] *Ber.*, 1919, 52, 753 ; *J.*, 1919, 410A.
[105] *J.*, 1919, 146A.   [106] *J.*, 1919, 28B.

SULPHUR.

The displacement of the sources of supply of this substance owing to the war is of interest.

The Texas Gulf Sulphur Co. has attained an output of 1200 tons per day, and contracted to export 200,000 tons a year from Texas City.[107]   American sulphur has displaced the Italian from the American market.   The Sicilian output continues to decrease (for 1917 it was 211,847 tons crude, 71,583 tons refined, and 44,320 tons ground—approximately one-half of the total for 1914).[108]   From the Japanese deposits, mainly in the island Hokkaido, 64,711 tons was obtained in 1918 ; this was 45·2% less than the 1917 output, and that for 1919 is expected to be lower still.[109]   The pre-war consumption of sulphur in Sweden was 40,000 tons yearly, most of which was imported from the United Kingdom and Sicily.   During the war Norwegian pyrites supplied the pulp mills, and there are prospects of American and Japanese sulphur entering this market.   Norway also imported sulphur from this country and from Sicily before the war and exported pyrites ; now the latter is largely used at home, and more than half the imported sulphur came from the United States in 1918.[110]

SELENIUM AND TELLURIUM.

About 10,000 lb. of selenium was produced in 1913 and 30,000 lb. in 1914, but much less since then.   Larger quantities could be obtained if necessary from anode slimes in copper refining.[111]

L. Ancel [112] describes the known uses of selenium, and L. M. Dennis and J. P. Koller [113] describe a laboratory method of preparing selenium from smelter fumes and anode slimes, and give methods of detecting tellurium and sulphur in it.   A. Gutbier and G. L. Weise [114] prepare colloidal solutions of selenium by electrolysis.

NITRIDES.

The nitrides of cobalt and nickel, Co_3N_2 and Ni_3N_2, can be obtained by dropping a mixture of the oxide and cyanide through an electric arc.[115]   They are not attacked by hot water, but yield ammonia when fused with caustic soda.

Cerium nitride, CeN_2, is formed when the metal is heated in air ; it yields ammonia with water.[116]

[107] Bd. of Trade J., July, 1919 ; J., 1919, 269R.
[108] J., 1919, 293R.   [109] J., 1919, 329R.
[110] U.S. Consular Rep., July, 1919 ; J., 1919, 340R.
[111] Metall und Erz, Dec., 1918 ; J., 1919, 126R.
[112] Chim. et Ind., 1919, 2, 245 ; A., 1919, 321A.
[113] J. Amer. Chem. Soc., 1919, 41, 949 ; J., 1919, 534A.
[114] Ber., 1919, 52, 1374 ; J., 1919, 679A.
[115] A. C. Vournasos, Comptes rend., 1919, 168, 889 ; J., 1919, 412A.
[116] P. Fabaron, Ann. Chim. Analyt., 1919, 1, 156 ; J., 1919, 412A.

ARSENIC.

Arsenic trichloride, 99% pure, is obtained by heating a mixture of arsenic trioxide and sulphur chloride at $100°$-$125°$ C.: $2As_2O_3 + 6S_2Cl_2 = 4AsCl_3 + 3SO_2 + 9S$. The yield is 93%, calculated on the sulphur chloride.[117]

C. Doremus [118] describes an internally fired rotatory kiln for roasting arsenical pyrites. The vaporised arsenic trioxide is collected by means of a Cottrell precipitator and contains 98% As_2O_3.

An amorphous modification of arsenic which is soluble in carbon bisulphide is obtained by reducing a solution of arsenious chloride in concentrated hydrochloric acid with stannous chloride.[119]

PHOSPHORUS.

An interesting account of the sources, production, and consumption of phosphates in the world prior to 1913 is given by J. Hendrick.[120]

The production of phosphate rock in Egypt began in 1910 and reached 125,000 tons in 1916; since then it has fallen off owing to shipping difficulties. The rock contains 60-70% of $Ca_3(PO_4)_2$, and is the only considerable source of phosphates worked in the British Empire.[121] Deposits of rather low-grade rock (14-16% P_2O_5) are reported at Saldanha Bay (South Africa)[122] The Tunisian output of 572,696 metric tons in 1918 was over 150,000 tons less than the output for 1917 owing to labour shortage, but exports increased by more than 245,000 tons to 720,193 metric tons,[123] which compares with exports over 2 million tons in 1913.[124]

Several patents have been granted in the United States for processes for heating phosphate rock with silica and carbon, or carbon alone, and collecting the vaporised phosphorus in the form of phosphoric acid (cf. J., 1917, 134). The manufacture of a concentrated fertiliser is of obvious importance in view of the high cost of railway transit from the manufacturing centres to the more remote agricultural districts. The tendency seems to be to return to the use of heat developed by combustion instead of electrical heat, otherwise the processes do not appear to present any very novel features.

CARBON.

V. Kohlschütter [125] contends that graphite is not crystalline, but is one of the amorphous forms of carbon.

The reaction of carbon monoxide and sulphur dioxide, which must

[117] R. C. Smith, J. Ind. Eng. Chem., 1919, 11, 109; J., 1919, 174A.

[118] Trans. Amer. Electrochem. Soc., 1919, 279; J., 1919, 628A.

[119] R. G. Durrant, Chem. Soc. Trans., 1919, 115, 134; J., 1919, 220A.

[120] J., 1919, 155B.   [121] J., 1919, 187B.   [122] J., 1919, 228B.

[123] J., 1919, 293B.   [124] J., 1919, 354B.

[125] Z. anorg. Chem., 1919, 105, 35, 121; J., 1919, 174A, 221A.

occur in many furnace operations, yields carbon dioxide and sulphur, an equilibrium being established, the position of which at $1000°$–$1200°$ C. has been studied by J. B. Ferguson.[126] Small quantities of carbonyl sulphide are also formed, a result in agreement with the experiments of A. Stock, P. Seelig, and W. Ottmann,[127] who have studied the reversible reactions $2COS \rightleftharpoons 2CO + S_2$ and $2COS \rightleftharpoons CO_2 + CS_2$. At $800°$ the first takes place rapidly and the second slowly, about 64% of the carbonyl sulphide being decomposed in equilibrium ; at $950°$ at least 70% of it is decomposed.

During the war carbonyl chloride was extensively used as a poison-gas. Its preparation from sulphuric acid and carbon tetrachloride has been studied by V. Grignard and E. Urbain [128] and by C. Mauguin and L. J. Simon.[129] The products depend on the concentration of the sulphuric acid ; the reactions may be represented by the equations :

$$H_2SO_4 + CCl_4 = COCl_2 + ClSO_3H + HCl$$
$$2SO_3HCl + SO_3 = S_2O_5Cl_2 + H_2SO_4$$
$$2SO_3HCl + CCl_4 = COCl_2 + 2HCl + S_2O_5Cl_2$$
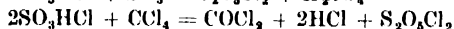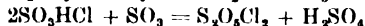
The change begins about $80°$ and is complete at $135°$–$140°$ C., the yield being 93–96% on the carbon tetrachloride used. The carbonyl chloride and hydrochloric acid formed are separated by washing with carbon tetrachloride, which dissolves phosgene, but very little hydrochloric acid.

SILICON AND TITANIUM CHLORIDES.

These compounds came into some prominence for the production of smoke clouds. The liquids were sprayed from a nozzle along with liquid ammonia. The titanium compound yields a denser cloud, but evaporates slowly and tends to choke the nozzle, so that silicon chloride was preferable.[130]

The preparation of this substance by the action of chlorine on carborundum at about $1200°$ C. is described by O. Hutchins.[131] The charge is heated to the reaction temperature by an electrically heated carbon rod, after which the temperature is maintained by the heat of reaction. A fire-brick chamber 3 ft. × 1 ft. produces 20–30 lb. per hour.

SODA.

The Le Blanc soda process is now obsolete.[132] The occurrence of a natural deposit of sodium and potassium carbonates is reported at

[126] *J. Amer. Chem. Soc.*, 1918, **40**, 1626 ; *J.*, 1919, 11A.
[127] *Ber.*, 1919, **52**, 681 ; *J.*, 1919, 413A.
[128] *Comptes rend.*, 1919, **169**, 17 ; *J.*, 1919, 574A.
[129] *Comptes rend.*, 1919, **169**, 34 ; *J.*, 1919, 575A.
[130] G. Richter, *Trans. Amer. Electrochem. Soc.*, April, 1919 ; *J.*, 1919, 412A.
[131] *Ibid.* ; *J.*, 1919, 412A.   [132] *J.*, 1919, 150B.

Klerksdorp (Transvaal),[133] and some details of the extraordinary Magadi soda lake in British East Africa are published.[134] Over 300 million tons of soda is said to be exposed ; the working of this deposit has been delayed by increased cost of labour and by difficulties of transit.

ALUMINA.

Labrador stone, a white rock, mountains of which occur in south-western Norway in the Sogne Fjord district, consists of a plagioclase felspar containing small quantities of iron-bearing pyroxenes. It contains about 30% of Al_2O_3, and H. Goldschmidt, of Christiania,[135] has devised an ingenious process for its utilisation. The rock is surprisingly soluble in dilute acids ; 30% nitric acid (from the arc process) dissolves CaO (13%), Na_2O (5%), and Al_2O_3, leaving a residue of silica and ferromagnesian minerals. The solution, on evaporation, decomposes, giving off nitric acid and leaving a residue of insoluble alumina together with soluble nitrates of sodium and calcium, which are utilised as fertilisers.

ALUMINIUM AND MAGNESIUM CHLORIDES.

The preparation of the anhydrous chlorides by the action of carbonyl chloride on the oxides at 350°–400° C. for $AlCl_3$, 500° 600° for $MgCl_2$, and 650° for $CeCl_2$ is patented by W. Heap and E. Newbery [136] and by G. H. King and G. I. Roberts [137]

The troublesome dehydration of magnesium chloride can be carried out, according to P. L. Hulin,[138] by burning chlorine and hydrogen in contact with it, thus supplying both the heat required and the atmosphere of hydrochloric acid needed to prevent decomposition.

PERMANGANATES.

As in so many other cases, the world's supplies of permanganates appear to have been largely of German origin up to 1914. The manufacture of permanganates, required, among other things, for use in box-respirators, has therefore received a good deal of attention. H. I. Schlesinger, R. D. Mullinix, and J. Popoff [139] show that when a finely powdered mixture of manganese dioxide and caustic potash is heated in air at 450° C., oxidation often stops when about 60% of the quantity of manganate calculated from the equation $4KOH + 2MnO_2 + O_2 = 2K_2MnO_4 + 2H_2O$ has been formed. The conversion into manganate really depends greatly on the quantity of potash used ; it increases

[133] J., 1919, 228E.   [134] J., 1919, 380E.
[135] Tidsskrift for Kemi, No. 2, 1919 ; Nature, 1919, 161.
[136] Eng. Pats. 130626 and 131039, 1918 ; J., 1919, 718A.
[137] U.S. Pat. 1308080 ; J., 1919, 630A.
[138] U.S. Pat. 1304567 ; J., 1919, 630A.
[139] J., Ind. Eng. Chem., 1919, 11, 317 ; J., 1919, 321A.

with the potash, reaching the theoretical value when $2\frac{1}{2}$ molecules of KOH are used to each molecule of MnO_2. Further increase in the quantity of potash diminishes the yield by converting the deep purple manganate into a green compound, $2K_2MnO_3,3K_2MnO_4,3K_2O$. Potassium carbonate is inert, and sodium hydroxide gives very much smaller yields than the potassium compound.

R. E. Wilson and W. G. Horsch [140] describe the preparation of sodium permanganate by electrolysis of a solution of sodium hydroxide with ferromanganese anodes enclosed in a diaphragm of asbestos paper.

THORIUM.

The diluted sulphuric acid extract of monazite sand, prepared in the usual way, is treated according to J. V. and W. A. Clarke [141] with permanganate until a permanent coloration results; thoria or the peroxide is precipitated. L. W. Ryan [112] precipitates the thorium as fluoride.

CERIUM.

The reduction of cerium oxide with carbon in the electric furnace takes place in three stages : $2CeO_2 + C = Ce_2O_3 + CO$; $Ce_2O_3 + 9C = 2CeC_3 + 3CO$; and $CeC_1 = CeC_2 + C$. The carbide CeC_3 forms solid solutions with the oxide Ce_2O_3 and only exists within narrow limits of temperature, readily dissociating into the lower carbide and graphite.[143]

ZIRCONIA.

A. J. Phillips [144] states that iron is best removed from zirconia by mixing it with 4% of petroleum coke and treating the mixture with moist chlorine at $900°$ C.

THALLIUM.

G. Sisson and J. S. Edmondson [115] found 0·25% of thallium (corresponding with 1 part per million of pyrites) in the flue dust from a pyrites burner using Spanish ore.

ACETIC ACID.

The manufacture of acetic acid from acetylene is reported to have been working successfully at Shawinigan Falls, Quebec, since 1916. Two plants exist, with a monthly capacity of 700–800 tons of glacial acid each.[146] The manufacture of the intermediate acetaldehyde in

[140] *Trans. Amer. Electrochem. Soc.*, April, 1919 ; *J.*, 1919, 411A.
[141] Eng. Pat. 120748, 1917 ; *J.*, 1919, 74A.
[142] U.S. Pats. 1307152 and 1307153 ; *J.*, 1919, 576A.
[143] G. Damiens, *Ann. Chim.*, 1918 [ix], 10, 330 ; *J.*, 1919, 174A.
[144] *J. Amer. Ceram. Soc.*, 1918, 1, 791 ; *J.*, 1919, 252A.
[145] *J.*, 1919, 70T.   [146] *J.*, 1919, 44B.

Norway is also reported.[147] S. Utheim [148] patents the oxidation of acetaldehyde by oxygen in narrow silver or aluminium tubes at pressures of 3 to 15 atmospheres and temperatures between 30° and 70° C., whilst H. Dreyfus [149] passes oxygen through the liquid aldehyde, which is vigorously agitated, at -10° to 0° C.

[147] J, 1919, 65R.   [148] Eng. Pat. 116279, 1918 ; J., 1919, 414A
[149] U.S. Pat. 1308173 ; J., 1919, 629A

GLASS.

By W. J. Rees, F.I.C.,

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DURING the year under review there has been considerable activity in the modernising and enlarging of existing plants and in the provision of new plant in order to cope with the great demand for all types of glassware which has manifested itself since the end of the war. The abnormal demand for illuminating glassware consequent on the removal of lighting restrictions redirected attention to our pre-war dependence on imported supplies, and it is satisfactory to record that the attention given by British manufacturers to this branch of the glass industry has been such that the supply should soon be as satisfactory in quantity as it already is in quality. If these new branches of manufacture are to be retained and developed in this country it is essential that interest in the scientific aspects of the manufacturing processes should not slacken. Production can be increased and quality improved by the application of scientific methods, and to this end co-operation between the chemist, the physicist, and the engineer will be of the first importance. The Department of Glass Technology of the University of Sheffield is developing into the technical headquarters of the industry, and it will be to the advantage of the industry to give to this Institution the financial support which its adequate and continued development will need. Its first volume of Collected Researches is an indication of its potential value to the glass industry in general. The formation of a Glass Research Association under the auspices of the Department of Scientific and Industrial Research is an event of great importance, and the large funds (£100,000) at its disposal will enable it to undertake a team work attack on those problems the solving of which is necessary to the security of the industry. The field to be covered is a large one, but among the most urgent problems are those connected with the use of mechanical glassware-making machinery, annealing, fuel economy, and the provision of improved refractories. Quite early in the war there was an awakening to the indispensability of the glass industry to many other industries, and there are now good grounds for the hope that a stable British glass industry will be firmly established. The Government have recognised the importance of

fostering such sections of the industry as those engaged in the production of optical glass and scientific and illuminating glassware by including them in the schedule of unstable " key " industries.

Definite progress in the introduction of automatic and semi-automatic glass-forming and glassware making machinery can be recorded. One large electric lamp-bulb works is now equipped with the Westlake automatic machine which has a capacity of 4000 bulbs per hour, and several others are equipped with such semi-automatic machines as the " Empire." Machines for the automatic production of lamp chimneys, tumblers, and many varieties of food containers are in course of installation and large outputs of bottles are being obtained both from Owens machines and from other smaller unit machines. The development of mechanical methods for sheet glass making is being followed with great interest and a factory is now in course of erection in this country for a large production of sheet glass by the Fourcault method in successful use in Belgium.

Gas fired furnaces are rapidly replacing the uneconomical direct coal fired furnaces in all sections of the industry. Increase of output is necessitating higher melting temperatures in tank furnaces and quicker founds (with consequent higher founding temperatures) in pot furnaces, and the economical production and control of these higher temperatures is receiving much attention from furnace engineers. Recuperative furnaces, with special reference to the Stein furnace, are discussed by J. A. Atkinson,[1] and attention directed to the advantages of vertical over horizontal recuperator passages. Very considerable claims for economy of fuel consumption are made for this furnace. It is desirable that some standard method of comparing fuel consumption with glass produced should be adopted. At present it is uncertain whether figures of fuel consumption given relate to batch melted, glass produced, glass drawn from the pot, or finished glass made. Information of definite value would be given if the fuel consumption per ton of glass batch melted and the composition of this batch (with proportion of cullet) were stated.

M. W. Travers[2] describes a gas fired furnace in which covered pots are set in separate arches arranged in pairs on either side of the gas producer. The gas entering through two ports in front of the pot meets the secondary air 8 inches below the bottom of the pot, combustion taking place in the arch in front of the pot, and the products of combustion passing round the pot and out through a flue in the top of the arch. With resistance glasses which are difficult to found, a high quality of glass was obtained and the cracking of the front of the pot, which is a fairly frequent cause of loss of pots in furnaces of the usual type in which the front of the pot is not heated, was avoided,

[1] J. Soc. Glass Tech., 1919, 3, 148.
[2] J. Soc. Glass Tech., 1919, 3, 70; J., 1919, 72vA,

This reversal of the more usual direction of flow of the gases through the furnace appears to be capable of extension to recuperative and regenerative furnaces, and as a longer pot life is obtained it should receive the attention of furnace engineers.

C. N. Fenner [3] discusses the use of optical pyrometers for the temperature control of glass-furnaces. Ordinary thermo-couples were found to be unreliable for the purpose, but satisfactory results were obtained by the use of an optical pyrometer of the Holborn-Kurlbaum type. In the writer's experience it has been found possible to obtain satisfactory control by the use of properly protected radiation pyrometers in conjunction with recorders, an optical pyrometer only being necessary for exact measurement of the temperature of the glass at any moment.

C. N. Fenner and B. Ferguson [4] investigated the occasional occurrence of milkiness in certain lead glasses and consider that it was due to the catalytic action of small proportions of sulphate and chloride in the impure Russian potash which was used causing the separation of clouds of minute crystals of cristobalite. W. E. S. Turner and J. D. Cauwood [5] have previously suggested that the presence of these particular impurities was liable to produce cloudy glass, but the new observation with the suggestion that the milkiness is due to cristobalite thrown out of solution is of particular interest, although the possibility of this formation of cristobalite at temperatures of 950–1000 C. is scarcely consistent with Fenner's observations [6] on the stability relations of cristobalite and tridymite.

E. W. Washburn [7] traces the green colour of a glass made from iron-free materials to the absorption of iron from the furnace atmosphere. As a remedy the use of iron-free bricks for lining the furnace and the water cooling of any iron used in the interior of the furnace, is suggested. The furnace used appears to have been of peculiar design, with iron burners, a change-over to clay burners considerably reducing the observed coloration. E. T. Allen and E. G. Zies [8] discuss the rôle of arsenic in glass-making and consider that the major part of it remaining in the glass is present in the quinquevalent condition. Their analyses show that from 10 to 30% of the arsenious oxide added is lost by volatilisation, and they suggest that a portion of it is oxidised at low temperatures, the product dissociating slowly at higher temperatures into oxygen and arsenic trioxide. This is in conformity with observations made by the writer that under certain conditions arsenic will act as an oxidising agent.

M. W. Travers [9] suggests that considerable advantages may be obtained by grinding the cullet and then thoroughly mixing it with

[3] J., 1919, 682A.   [4] J. Amer. Ceram. Soc., 1918, 1, 468 ;   J., 1919, 105A.
[5] J., 1917, 387.   [6] J. Soc. Glass Tech., 1919, 3, 124 ;   J., 1919, 722A.
[7] J. Amer. Ceram. Soc., 1918, 1, 637 ;   J., 1919, 137A.
[8] J. Amer. Ceram. Soc., 1918, 1, 787 ;   J., 1919, 254A.   [9] J., 1918, 235T.

the batch Attention is also directed to the importance of the pheno
mena relating to the formation of "cords" in glass At times during
the working of a pot of metal the glass becomes and remains " cordy,"
but it occasionally becomes clear again in a remarkable manner
Travers suggests that this may be a surface phenomenon and should
receive attention from investigators of the behaviour of colloids
N L Bowen [10] deals generally with various factors tending to produce
non-homogeneity From observations made it is suggested that the
more fusible portions of the batch liquefy and enter downward through
the less fusible material Usually the sand was the last material to
dissolve, the grains tending to rise in the already fluid portion making
the upper parts more siliceous and of lower density This density
gradient was gradually lessened by diffusion and could be eliminated
by stirring The action described could be observed at an intermediate
stage, sand grains being then found suspended in the liquid with a tail
of glass of lower refractive index than the surrounding glass pointing
down from each grain Other factors such as solution of the pot and
the volatisation of certain ingredients of the batch are considered to be
of less importance in their effect on homogeneity The present writer
would emphasise the importance of proper founding temperatures in
lessening the time required to reduce the heterogeneity produced by
differential melting of the batch ingredients

Bowen [11] in a further paper classifies particles of a non vitreous
nature occurring in glass as pot stones batch stones crown drops and
devitrification stones according to their origin as determined by micro
scopical examination Sillimanite is found only in stones which originate
from detached fragments of the pot (or tank block) Batch stones
were found to be almost invariably unmelted sand and may consist
of a core of unchanged quartz surrounded by a layer of tridymite or
cristobalite, or if the grain is small it may be completely converted to
tridymite or cristobalite A batch stone usually is surrounded by an
aura, and generally has a "tail" also of glass of lower refractive index
than the body of the glass This "tail" is absent in devitrification
stones Crown drops are due to the falling into the glass of drops of
fused or corroded material from the crown of the furnace In the case
of a silica crown such particles usually consist of rather large crystals
of tridymite. Devitrification stones are usually spherulitic and may
consist of tridymite, cristobalite, wollastonite barium or lead silicate,
according to the nature and composition of the batch Proper balancing
of the batch or special heat treatment will reduce the liability to the
formation of these stones in a particular glass

The same author [12] deals further with the phenomena of devitrifi-

[10] *Optician*, 1918 193
[11] *J. Amer. Ceram. Soc.*, 1918, **1**, 594; *J.* 1919 938A.
[12] *J. Amer. Ceram. Soc.*, 1919, **2**, 261, *J.* 1919, 509A.

cation and refers to the point that the composition of a glass must be such that it does not become supersaturated with any components at any temperature at which it may require to be maintained. To prevent crystallisation of silicates a glass must be cooled rapidly to a point where the crystallising power of these substances is negligibly small. In a glass which is to be reheated for working or annealing, the upper limit of temperature at which devitrification can occur is important. This temperature is determined by maintaining a piece of devitrified glass at a certain temperature for 1 hour, chilling it rapidly, and examining it. This is repeated at successively higher temperatures until one is found at which all traces of crystals have disappeared. The moulding temperature for a glass should be slightly higher than that found by this method.

M. Luckiesh [13] describes methods for utilising spectral analysis for the development of coloured glasses. Chemical considerations may alter the predictions based on computation, but the procedure outlined will form a working basis. Spectral analyses of some fundamental coloured glasses and some simple combinations are presented. Cobalt, which is commonly used for blue glass, transmits a deep red band also, but if a cobalt blue is combined with copper bluish-green, the latter absorbs the red and an excellent blue glass is obtained. It is considered in such cases as street-lighting glassware undesirable to " decolorise " the glass by the use of manganese to neutralise the green tint due to iron impurity because of the consequent reduction of the transmission factor. In developing a coloured glass for a specific purpose it is essential that the illuminant to be used should be considered

OPTICAL GLASS.

War-time efforts to introduce the manufacture of optical glass into America were considerably assisted by experimental work carried out by the staffs of the Geophysical Laboratory and the Bureau of Standards. C. N. Fenner [14] and N. S. Williams and C. C. Rand [15] deal generally with the procedure necessary for the production of homogeneous glass. Batch compositions for various types of glass are given, and the precautions necessary in founding are referred to in detail. A small quantity of ammonium nitrate wrapped in paper, immersed and held near the bottom of the pot by an iron rod, is stated to be specially suitable for " plaining " optical glasses. The technique of the stirring operation is discussed in detail. Well-burned fireclay stirrers, operated by a machine-driven water-cooled stirring rod, are used. At the end of the stirring, the clay stirrer is drawn to the side of the pot and held there by an inverted U-bar ; if lifted out of the glass its removal tends

[14] *J. Franklin Inst.*, 1917, **184**, No. 1.
[14] *J. Amer. Ceram. Soc.*, 1919, **2**, 102 ; *J.*, 1919, 361A.
[15] *Ibid.*, 422 ; *J.*, 1919, 632A.

to produce striæ Fenner does well to emphasise the necessity of attention to details The whole process must be treated as a large scale laboratory operation in order to obtain the necessary quality and uniformity of product G W Morey [16] from experimental work undertaken at the optical glass plant of the U S War Industries Board suggests that the time required to " found " a pot of optical glass completely may be reduced to 24 hours by commencing stirring as soon as the pot is half full of molten glass instead of waiting until it is full and the metal plain The modification is such a revolutionary one that although 350 satisfactory pots of various types of glass are stated to have been made by the method, the present writer would not express an opinion on its soundness without comparing the general quality and homogeneity of the glass produced with that made under the normal procedure in Europe If the claims made for it are substantiated by the production of glass equal in quality to that of British optical glass then a great step forward has been made but the writer is under the impression that the quality of American war time optical glass left much to be desired In this country, progress in the production of all types of optical glass, including those of extreme optical properties has been continuous during the year and the British optician will now be completely independent of foreign supplies

Scientific and Illuminating Glassware

The majority of the problems involved in the large scale production of these types of glassware have been solved Generally speaking, the mechanical and chemical durability of home produced laboratory glassware is satisfactory, but it is desirable to direct the attention of manufacturers to such inequalities of thickness due to uneven blowing, as may cause breakage when, for instance a water filled beaker is lifted

W E S Turner and J D Cauwood [17] in a continuation of their work on the resistant properties of chemical glassware have examined the effect of temperature on the rate of corrosion From a series of carefully controlled tests it is shown that in all cases the corrosion increases rapidly with rise of temperature With water, the dissolved matter is doubled for each rise of 5 C between 90 and 100 C , with 2N sodium carbonate the attack was doubled for each rise of 10 C between 60° and 100 C , but with 20% hydrochloric acid the rate of increase in chemical action with temperature was distinctly less than with water and alkali.

R G. Sherwood [18] suggests that the gaseous evolution when glass is heated is of two different kinds, viz , that resulting from adsorption,

[16] J. Amer. Ceram. Soc., 1919, **2**, 146; J., 1919, 364A.
[17] J. Soc. Glass Tech., 1918, **2**, 200; J., 1919, 139B.
[18] J. Amer. Chem. Soc., 1918, **40**, 1645; J., 1919, 13A.

which is readily removed at temperatures below 300° C., and that due to a decomposition of the glass itself. The latter effect becomes important at 400°–500° C., depending on the nature of the glass.   The decomposition products are carbon dioxide and monoxide, hydrogen, nitrogen, and water, the latter being the principal product at temperatures near the softening point of the glass.   In heating a hard glass vessel which has been annealed at 600° C., there is little or no evolution other than that of adsorbed gas until after this annealing temperature has been passed.

A representative Committee formed on the initiative of the Society of Chemical Industry has considered the question of the Standardisation of Laboratory Glassware.   Important recommendations are made in the report of this Committee [19] with regard to the dimensions of pipettes and burettes and all types of mould-blown apparatus, and their general adoption will be an advantage to both maker and user.

Annealing

M. W. Travers [20] refers to the difficulties presented by the annealing of scientific glassware because of the large bulk for small weight which has to be dealt with   As the goods must pass very slowly through the hot part of the lehr, large lehr accommodation is necessary.   The use of gas-fired lehrs is recommended, the fall of temperature being controlled by taking away the hot gases into a flue through openings with movable dampers   Resistance glass, it was found, could be removed from the lehr at 300 C.   S. English and W. E. S. Turner [21] have ascertained the effect on the annealing temperature of variations in composition of lime-soda glasses   As the proportion of lime increases, the annealing temperature also rises.   The annealing temperature of a glass with 15–17% of soda, 7–9% of lime, and about 74% of silica will be between 538 and 562 C., that of a glass with 13% of soda and 11·6% of lime is 601 C., whilst that of a glass with 11% of soda, 17% of lime, and 69% of silica is 613° C. As the same authors have previously shown that an alteration of 5° C. in the neighbourhood of the annealing temperature has a large influence on the speed of annealing, it is obvious that proper adjustment of the lehr to the particular glass is of great importance.   Troubles from defective annealing most frequently arise where a compromise in lehr temperature is adopted and glasses differing in chemical composition are passed through the lehr together.

W. P. White [22] in a continuation, of investigations on the specific heats of silicates, has determined the mean specific heats of cristobalite, anorthite, andesine, albite, microcline, wollastonite, diopside, mag-

J., 1919, 280 R.   [20] *J.*, 1918, 235T.
J. Soc. Glass Tech., 1919, **3**, 125 ; *J.*, 1919, 722A.
[22] *Amer. J. Sci.*, 1919. **47**, 1 ; *J.*, 1919, 140A.   See also *J.*, 1909, 1127.

nesium silicate amphibole, and magnesium silicate pyroxene for eight intervals ranging from 0 100° C to 0 1400° C. The mean specific heats of silica and these silicates was also determined in the glassy form, and it was found that the specific heat of the glass is seldom greater than that of the crystal. The exceptions occurred in the glasses containing sodium and potassium and might be connected with the fact that these substances tend to give high expansion coefficients to glasses in which they occur. For quartz and silica glass the values of the interval specific heats satisfy the expressions

Quartz 0·1685 + 0·0001940 0·00000110²
Silica glass 0·1670 + 0·0001890 0·00000125θ²

E. W. Tillotson [23] in investigating the relation between the physical properties and chemical composition of glass, refers to the formation of molecular compounds. The graph representing the variation of the refractive index or specific gravity of a glass with the composition consists of one or more straight lines; when there is more than one line the points of intersection indicate the composition of molecular compounds. Glasses composed of mixtures of albite and anorthite give a single line graph, but the graphs of mixtures of calcium and magnesium orthosilicates form three straight lines intersecting at two points indicating the formation of two compounds, $CaMg_2(SiO_4)_2$ and $Ca_3Mg(SiO_4)_2$. No indication is given of the formation of diopside, $CaMg(SiO_3)_2$, which is the only double silicate crystallising from these mixtures. Graphs are plotted showing the relation of the refractive index to the composition of glasses of the systems Na_2O-BaO-SiO_2 and Na_2O-CaO-SiO_2. In the latter the existence of only one ternary compound $2Na_2O.3CaO.7SiO_2$ is indicated. A lime soda glass corresponding to $12Na_2O.3CaO.45SiO_2$ is therefore considered to be a solution of 1 mol. of $2Na_2O.3CaO.7SiO_2$, 10 mols. of $Na_2O.2SiO_2$, and 18 mols. of SiO_2, and a higher melting point glass corresponding to $Na_2O.CaO.6SiO_2$, a solution of 1 mol. of $2Na_2O.3CaO.7SiO_2$, 1 mol. of $Na_2O.2SiO_2$, and 9 mols. of SiO_2. Tillyer suggests that a hyperbolic curve fits Tillotson's experimental results just as well as intersecting straight lines and that such a curve does not indicate the formation of any of the suggested compounds.

[23] *J. Amer. Ceram. Soc.*, 1918, 1, 5. *J.*, 1919, 13A.

REFRACTORIES.

By W. J. Rees, F.I.C.,

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The increasing volume of research work on refractories is indicative of the greater interest displayed by both manufacturer and user in the provision of refractory materials properly suited for the service they have to perform. In the metallurgical, gas, glass, and coke industries, efficiency and economy of production are to no small extent dependent on the durability of the refractory materials used. In all these industries there is a definite need for refractories which will better withstand the severe conditions imposed by higher furnace temperatures and increasing output. Especially is this the case in the smelting of steel and alloys in the electric furnace. Progress in the design of electric furnaces is very largely dependent on the provision of refractories which will adequately perform the service asked of them. Co-operation between the research worker, the manufacturer, and the user is the first essential to progress, and this will be assured in the Refractories Research Association which has been formed on the initiative of the Refractories Section of the Ceramic Society. Under the direction of Dr. J. W. Mellor (from whose laboratory at Stoke a great portion of the refractories research in this country has issued) an organised scheme of research on an adequate scale is to be proceeded with immediately It is vitally necessary that this Association should receive the whole-hearted support of the makers of refractories so that funds may be available for the complete programme of work which has been mapped out. The Department of Scientific and Industrial Research is supporting the scheme to the extent of doubling all funds subscribed, and although this is not such generous assistance as has been accorded to glass research it should encourage the manufacturers to avail themselves to the fullest extent of this opportunity to obtain the benefits of collective research. The Glass Research Association also proposes to undertake research work into such refractories as are necessary in glass manufacture, and to carry on the work initiated by the Refractories Research and Specifications Committee of the Society of Glass Technology. Co-operation between the two Associations in this phase of refractories research is desirable and will doubtless be arranged. An extended research into the problems underlying the constitution of moulding sands is desirable. Prof. Boswell's pioneer work during the

war has cleared the way and indicated the particular points on which knowledge is lacking. Our resources of naturally bonded sands which are suitable for steel moulding are much smaller than those which are at hand for iron and non-ferrous foundries. A continuance of the search for new resources of suitable steel moulding sands is necessary, but even more essential is the further development of research to elucidate the factors which give to suitable naturally bonded sands their precise properties, so that it may be possible, when necessity arises, to replace such sands by synthetic mixtures of a high silica sand with a clay or other form of colloidal bond. Our known home resources of sands which are as suitable for steel casting as the French and Belgian red and yellow moulding sands are very limited. This and the increasing production of high grade steel castings, with the consequent greater demand for satisfactory moulding sands, apart from the point of view of national security, emphasises the urgency of the situation.

Silica Refractories

H. le Chatelier and B. Bogitch [1] have continued their experimental work in connection with the improvement of silica bricks, and suggest a number of tests for controlling the quality. Their previous work showed the advantages derived from the presence in the brick mixture of a proportion of impalpable ground silica, and they now consider that the proportion of the material which will pass a 200-mesh sieve should not be less than 25%. There is little doubt that the contention that variation in the proportion of silica flour present is the commonest cause of variation in the quality of bricks, is correct. Attention is directed to the moisture contents of the " green " bricks, as the use of a too dry mixture tends to produce weak and laminated bricks. In the burning of the bricks it is suggested that the expansion of the bricks at various points in the kiln should be measured; this is a common practice at several English works with which the writer is acquainted and is a desirable check on uniformity of burning. As a rapid test of the chemical composition of a brick, the proportion of sulphates left after treatment of a prepared sample with hydrofluoric and sulphuric acids is adopted; this proportion should not exceed 10%. The efficiency of the burning in producing inversion of the silica is checked by a specific gravity determination; these should be between 2·30 and 2·40. For measuring the crushing strength the Brinell ball test is used [2]. It is rightly considered that the expansion and the loss of crushing strength on heating to 1600° C. indicate the probable behaviour of the bricks when in use in steel furnaces and the authors have devised tests for determining these factors. R. J. Montgomery and L. R. Othe [3] in discussing the laboratory testing of silica bricks suggest that

[1] Rev. Mét., 1918, 15, 511. [2] 1919, 222s. [3] J. 1918, 373A.
[3] J. Amer. Ceram. Soc., 1918, 1, 335; J., 1919, 15A.

the load test denned by the American Society for Testing Materials (25 lb. per sq. in. at 1500° C.) is of doubtful value as failures are usually due to a shearing or rupture of the bond and not to lack of refractoriness. In the writer's opinion a test of this type is of considerable value as a measure of the quality of the brick mixture and the efficiency of the burning. With a properly graded and compounded mixture, an interlocking network of recrystallised silica is produced throughout the brick matrix on adequate burning, and this gives satisfactory strength and durability to the brick at high temperatures.

L. Dauphin [4] confirms that the effect of iron oxide on the refractoriness of a silica brick is much more marked in the presence of high lime or high alumina.

C. N. Fenner [5] has amplified his previous work on the stability relations of the crystalline modifications of silica. Methods for the identification of the different forms are described and discussed, and new experimental work is considered in detail. The sluggishness of the inversions between quartz, tridymite, and cristobalite calls for the use of methods of investigation giving definite assurance that the modification found is that which is stable for the given conditions. Much of the argument against the validity of Fenner's conclusions from his earlier work on these stability relations has been based on the fact that the transformations were observed on separation from a particular flux (tungstate of soda) and on the observations of Le Chatelier and others that tridymite is an important constituent of those portions of a silica brick which have been at temperatures above 1480° C. in industrial furnaces. Fenner's earlier conclusions are considerably strengthened by this new experimental work. At temperatures above 1470°±10° C., quartz, tridymite, and amorphous silica have been converted into cristobalite; between 1470° and 870°±10° C., quartz, cristobalite, and amorphous silica have been converted into tridymite : and below 870° C., tridymite, cristobalite, and amorphous silica have been converted into quartz. These results, and the observation of J. B. Ferguson and H. E. Merwin [6] that the melting point of tridymite is decidedly below that of cristobalite, place beyond doubt the fact that (at any rate under all normal conditions) at temperatures above 1480° C., cristobalite is the stable form of silica.

From the point of view of the maker and user of silica bricks, it is desirable to have more definite information on the extent to which the sluggishness of the rate of inversion of quartz is modified by the presence of particular fluxes, and on the effect on the behaviour of the brick of the presence of those fluxes. Accurate observations of the works' behaviour of silica bricks containing all or much of the silica

[4] *Bull. Soc. de l'Ind. Min.*, 1918, **18**, 137; *J.*, 1919, **136A**.
[5] *J. Soc. Glass Tech.*, 1919, **3**, 116; *J.*, 1919, **722A**.
[6] *Amer. J. Sci.*, 1918, **46**, 417; *J.*, 1918, **546A**.

in the form of tridymite or cristobalite are also necessary in order to obtain trustworthy data for brick making purposes. The thermal treatment of a silica brick in its early life in a furnace may possibly be of more importance than the precise proportions of quartz, tridymite, or cristobalite present, and the physical structure of more importance (within limits) than the mineralogical or chemical constitution of the brick.

Fireclay Refractories.

R. E. Somers[7] describes in detail the properties of the minerals present in clays by which they may be identified in a macroscopical examination. Information of much practical importance is yielded by such an examination of both the raw clays and the fired article particularly when it is accessory to a chemical analysis. In clays which have been fired up to 1300° C. the author observes that quartz grains are more clearly visible than in the raw clay. hydromicas disappear or lose the greater part of their interference colour when heated to 1150° C. whilst kaolin appears to retain its shape and much of its interference colour. tourmaline and epidote disappear at 1150° C. but rutile, zircon, and titanite appear to be unaffected at 1300° C. A double refraction was observed in the ground mass of some clays fired at high temperatures. The mineralogical composition of a large number of American clays is shown in tabular form.

A. B. Jameson[8] has examined a number of New Zealand clays using the method of "rational" analysis devised by Zschokke[9]. Processes of this type cannot be recommended as a general method for comparing the properties of different types of clays though they may be of assistance in forming a rough idea of the mineralogical composition of clays. In the case of high grade refractory clays the rational or mineralogical composition can be calculated with sufficient accuracy from the ultimate analysis. H. S. Washington[10] suggests a simple method for calculating the mineral composition of clays from the ultimate chemical analysis. In a comparison of a series of rational and chemical analyses of clays, the lack of agreement between the two methods of analysis is very apparent and the unreliability of the so-called rational analysis is obvious.

The Ceramic Society Committee on the Standardisation of Tests or Refractory Materials[11] have proposed a standard method for the grading of clays according to the size of grain. The clay particles are separated into groups having specified limits, the sizes of the par-

[7] J. Wash. Acad. Sci., 1919, 9, 113; J., 1919, 251A.
[8] N.Z. J. Sci. Tech., 1919, 2, 209; J., 1919, 632A.
[9] Baumaterialenkunde, 1902, 7, 149.
[10] J. Amer. Ceram. Soc., 1918, 1, 405; J., 1919, 165A.
[11] Trans. Ceram. Soc., 1918, 18, 251; see J., 1918, 694A.

ticles in each group being determined by sieve analysis (using I.M.M. standard lawns) and elutriation.

In using a pug-mill for the preparation of clays, over-pugging may cause unsoundness by the excessive introduction of air ; the blades of the pug-mill should be set so as to give the maximum soundness to the tempered clay. H. Spurrier [12] describes a simple method for the determination of air in plastic clay. A sample of filter-pressed clay was found to contain 9·61% (by vol.) of air ; the same clay after pugging contained 9·88%, and after passing five times through the pug-mill, 13·8% of air.

GLASSHOUSE POTS AND TANK BLOCKS.

The development in the use of gas-fired furnaces and the necessity for the use of higher founding temperatures for producing resistant and other glasses and for increasing output have resulted in focussing attention on the need for improving the efficiency of the glasshouse pot. In the past, too little attention has been given to the physical and chemical constitution of the clay pot, but a determined effort is now being made to solve the problems involved in specifying the physical and chemical properties desirable in a pot for general use or for a specific purpose. The Refractories Research Committee of the Society of Glass Technology [13] have published provisional specifications for the raw materials for use in making glasshouse pots and tank-blocks. The provisional specifications are based on the best present-day practice, but appended to them are a series of recommendations and suggestions to both maker and user with regard to processes of preparation and treatment of the raw materials which may lead to the desired improvements. For the making of glass-pots, three grades of clay are suggested. Grade III. approximates to the present average supplies of raw pot clay and glass-pots, and Grades II. and I. indicate superior compositions.

Tank blocks should have a physical structure which will resist penetration and a composition which will result at the temperature of use in the formation of a chemically resistant skin on the surface of the block in' contact with the glass. It is suggested that they should be made from—

(a) An aluminous bind clay containing little free silica, 36-40% alumina, less than ·2·5% alkalis, and· less than 4·5% of total fluxes and with a low sintering temperature and a refractoriness not below cone 31.

(b) A base clay containing 25 32% of alumina, less than 1·4% of alkalis, and 4·0% of total fluxes, and not less refractory than cone 31.

(c) Grog made by mixing (a) and (b) in a finely ground condition, tempering, making into rough bricks, and burning to cone 14.

[12] *J. Amer. Ceram. Soc.*, 1918. **1**, 710 ; 1919, **2**, 490 ; *J.*, 1919, 176A, 633A.
[13] *J. Soc. Glass Tech.*, 1918, **2**, 272 ; 1919, **3**, 1 ; *J.*, 1919, 137A, 463A

	GRADE I			GRADE II			GRADE III		
	Bind clay	Base clay	Grog	Bind clay	Base clay	Grog	Bind clay	Base clay	Grog
*Silica %	60 (a)	55 (a)	50 (a)	65 (a)	60 (a)	80 (b)	70 (a)	70 (a)	70 (a)
*Alumina %	34 (b)	40 (b)	40 (b)	30 (b)	35 (b)	35 (b)	25 (b)	25 (b)	25 (b)
*Ferric oxide %	1 (a)	1 (a)	1 (a)	2 (a)	2 (a)	2 (a)	2.5 (a)	2 (a)	2 (a)
*Na₂O and K₂O %	1.5 (a)	1.5 (a)	1.5 (a)	2 (a)	1.8 (a)	1.8 (a)	2.5 (a)	1.8 (a)	1.5 (a)
*MgO and CaO %	1.0 (a)	0.5 (a)	0.5 (a)	1 (a)	0.6 (a)	0.6 (a)	1.0 (a)	1.0 (a)	1.0 (a)
Refractoriness (cone)	32	35	35	30	32	32	28, 29	30, 31	31
Ground to	30 mesh (d)	30 mesh	10 mesh	30 mesh (c)	30 mesh	10 mesh	12 mesh	12 mesh	10 mesh
Calcining temperature (cone)	—	—	14 (b)	—	—	12 (b)	—	—	9 (b)

Na_2O and K_2O; MgO and CaO

* = Determined in the fired samples
(a) = and under.
(b) = and over.
(c) = When blunged it must not leave more than 10%, residue on a 30-mesh sieve.
(d) = When blunged it must not leave more than 10%, residue on a 30-mesh sieve.

The specifications received the general approval of the pot-clay suppliers, but the suggestions and recommendations have met with severe criticism, as it is considered that clays of the compositions specified for the higher grades are unobtainable, and that to comply with the general physical requirements of these grades would necessitate the scrapping of the existing clay-works plant. There is no doubt that to comply with the Grade I. suggestions will be difficult, but although it may be impossible for an individual pot-clay maker to obtain the necessary clays from his own resources, it will be possible to approach the indicated compositions by the blending of clays from the known resources of the United Kingdom, or by the purification, and subsequent blending, of clays by mechanical or other methods already available. The provision of plant necessary is purely an economic question. It will be to the advantage of the glassmaker to pay a higher price, if such is necessary, for clays, pots, and blocks which will have the required increased efficiency.

Both in this country and in America, increased attention is being directed to the making of glass-pots by the process of slip-casting. The method of slip-casting devised by Weber has been in satisfactory use for nearly 20 years in Germany, and there should be no great difficulty in adapting similar methods for use with British fireclays. The characteristics of a casting slip depend on the grading, proportions, and composition of the raw clays and grog used and on the nature and amount of deflocculent used. Its viscosity should be such that any settling of the grog is avoided.

F. H. Riddle [14] describes a plant used for the casting of ten pots of 5 cwt. capacity per day. To determine the viscosity of the slip, a flow viscometer of 1 gallon capacity with a discharge nozzle not less than ⅜ in. diam. is used. In the Weber process, the viscosity is compared with a standard, by measuring the current necessary to drive the agitator freely in the mixing vat.

J. W. Wright and D. H. Fuller [15] in dealing with the casting of porcelain glass-pots, give details of the composition of the slip which gave the most satisfactory results. They consider that the sp. gr. of the slip should be between 1·90 and 1·95, and that the best deflocculent is a mixture of carbonate and silicate of soda in the proportion of 3 to 4 ; from 0·20 to 0·33% being used. B. J. Allen [16] in discussing the manufacture of glasshouse pots, describes a variant of the Osmose process for purifying the clays used. A vacuum casting process is used by this author, rendering unnecessary the use of a core to the mould. The defect in pots made by this process is in the roughness of the interior surface of the pot.

[14] *J. Amer. Ceram. Soc.*, 1919, **2**, 647 ; *J.*, 1919, 766A.
[15] *ibid.*, 1919, **2**, 659 ; *J.*, 1919, 766A.
[16] *J. Soc. Glass Tech.*, 1919, **3**, 78 ; *J.*, 1919, 720A.

E. A. Coad-Pryor [17] describes experimental work designed to determine the mechanism of the corrosion of glass-pots, carried out at the National Physical Laboratory. It is deduced from the results, that the corrosion is largely due to abrasion. A development of this work is described by W. Rosenhain [18]; it is considered that the greater attack on the bottom and lower part of the sides of the pot is due to the effect of the circulation set up in the molten glass, there being an upward flow at the sides of the pot and a downward flow nearer the centre. The marked effect on the rate of pot-attack of relatively small changes of temperature is emphasised, and it is suggested that it would be a simple matter to determine, for any given glass and any given pot material, a curve connecting rate of pot-attack with temperature The presence of defects and variations in the texture of pots was examined by means of X-rays. In an unfired pot, iron compounds show as dark spots against a light background of clay, but in a fired pot they have a light central region and a darker rim Air bubbles and cavities are easily recognised

J. C Hostetter, H S Roberts, and J B Ferguson [19] suggest the removal of iron from glass pots (those used for optical glassmaking in particular) by volatilisation by chlorine at high temperatures Where it is impossible to obtain pot-making materials sufficiently free from iron for the founding of a specially corrosive glass, some such process might be desirable, but the increased porosity produced in the pot would probably introduce factors equally or more serious in effect on the quality of the glass than the original iron in the pot

M. F Beecher [20] in studying light-weight clay refractories compared their behaviour with that of full-weight firebricks The light-weight bricks were made by adding sawdust to the clay-grog mixture, the sawdust having much the same effect on the working properties of the mixture as the addition of grog. At least 45% of plastic clay was found necessary and the maximum practical amount of sawdust was about 40%. The weight of the bricks is controlled mainly by the amount of sawdust added, the porosity of the burned bricks increasing by an amount equal to half the bulk volume added. It is considered that the best single test for light-weight bricks is to determine the deformation at 1350° C. under a load of 50 lb. per sq. in. Most of the light-weight bricks examined showed less deformation than commercial full-weight bricks. Clare considers that ground cork ($\ge$ 16 mesh) is more satisfactory than sawdust as not only does it give a more uniform product but 50% of it may be safely added.

[17] *J. Soc. Glass Tech.*, 1918, **2**, 285 ; *J.*, 1919, 138A.
[18] *Ibid.*, 1919, **3**, 93 ; *J.*, 1919, 720A.
[19] *J. Amer. Ceram. Soc.*, 1919, **2**, 356 ; *J.*, 1919, 578A
[20] *Ibid.*, 1919, **2**, 336 ; *J.*, 1919, 578A.

J. A. Audley [21] has very usefully reviewed the refractories used in the zinc industry. Analyses are given of the materials used for retort building for the distillation of zinc in Silesia, Belgium, and America and also of a number of broken retorts. As the charge is usually basic, it is desirable to use clays containing only small proportions of free silica. Pulverised coke is a frequent addition to the clay mixture; it is considered that by this addition the life of the retort is increased and its permeability to zinc vapour reduced. The permeability is also reduced by externally glazing the retorts. Where siliceous ores are smelted, highly siliceous clays or clays admixed with sand or crushed quartzites have been successfully used for making the retorts. The mechanism of the corrosion of the retorts is discussed, the blue coloration being shown to be due to the formation of blue zinc spinel.

M. G. Babcock [22] considers that the retorts should have a porosity not exceeding 5% at 1300°–1400° C. and refers to the glazing of the retorts with mixtures of fluorspar and zinc sulphate or of soda, flint, and fluorspar, in order to reduce their permeability. In the furnaces, trouble has been experienced due to the contraction of the firebricks at the high temperatures now employed. This has been overcome to some extent by the use of composite bricks of refractory clay and crushed silica rock or by using firebricks in which both the grog and the brick itself are made from selected clays and burned at temperatures higher than those usual in ordinary firebrick making.

R. M. Howe [23] emphasises the marked influence of increases of temperature on the penetration of slags in refractories; in cases observed, an increase of 100° C. nearly doubled the area of penetration. J. W. Mellor has devised a slag penetration test [24] in which the slag is contained by a refractory ring which is cemented to the face of the brick under test. A method of this type possesses distinct advantages over methods in which the slag is contained by a hole bored in the brick, in that the *skin* of the brick is retained.

G. A. Loomis [25] in discussing the load-testing of firebricks shows that bricks which are notably expanded and overburned below 1425° C. invariably fail under the load test. It is suggested that the changes in volume and porosity of bricks between 1350° and 1425° C. give a reliable indication as to their ability to pass the load test and that the determination of these changes in volume and porosity before and after burning the samples at 1400° C. is quicker, simpler, and less costly than the load test.

W. Emery and J. W. Mellor [26] have shown that the crushing strength -

[21] *Trans. Ceram. Soc.*, 1918–1919, **18**, 43.
[22] *J. Amer. Ceram. Soc.*, 1919, **2**; 81; *J.*, 1919, 365A.
[23] *Chem. and Met. Eng.*, 1919, **20**, 167; *J.*, 1919, 255A.
[24] *Trans. Ceram. Soc.*, 1919, **18**, 516.
[25] *J. Amer. Ceram. Soc.*, 1918, **1**, 384; *J.*, 1919, 105A.
[26] *Gas J.*, 1919, **146**, 619; *J.*, 1919, 537A.

(as determined by the Standard test) of firebricks is reduced by increasing the size of the grog when the proportion of grog is constant, and also by increasing the proportion of grog when its size remains constant. It is suggested that there is probably a close relation between the temperature coefficient of vitrification and crushing strength and that it is likely that the crushing strength reaches a maximum during the burning of the brick and gradually diminishes when the brick is in use.

E. Czakó,[27] in discussing the thermal conductivity and specific heat of refractories, suggests that Wologdine's values [28] for the thermal conductivities are too high and that Goerens' conclusion [29] that the conductivity decreases with increasing porosity does not hold generally. The values of the thermal conductivities between 0° and 1000° C. of firebrick, fireclay-silica, and silica bricks are tabulated and a table is also given of recent determinations of the true and mean specific heats of firebrick and silica bricks at intervals of 100 C. between 0° and 1300° C. The specific heats increase with increase of temperature, the increase between 0° and 1300° C. being about one-third of the value at the lower temperature.

H. le Chatelier and B. Bogitch [30] refer to the unsatisfactory behaviour of bricks made from bauxite and other highly aluminous materials such as corundite (fused bauxite) when used in such structures as the roofs of steel furnaces. It is shown that these bricks readily deform at temperatures between 1200° and 1500° C. Although the alumina itself is infusible at steel-making temperatures, it is floating in a molten magma, and the brick consequently lacks that cohesion which is present in silica brick owing to the formation of a lattice structure of recrystallised silica. For special purposes, these authors have made highly refractory bricks, etc., from a mixture of 80% of pure calcined alumina with 20% of white bauxite, moulded under pressure and burned at 1700° C.

BASIC REFRACTORIES

The properties of basic refractory materials which chiefly affect their value for furnace use are their resistance to slaking, erosion, and corrosion.

J. S. McDowell and R. M. Howe [31] have made a series of comparative tests of the behaviour of dead-burned magnesites and calcined dolomites. Their results indicate that to ensure a high resistance to air-slaking the lime content should be low and iron oxide, alumina, and silica not excessive. The behaviour of calcined dolomite granules which had been well coated at a high temperature with open-hearth

[27] J. Gasbeleucht , 1919, 62, 274 ; J., 1919, 634A.
[28] J., 1909, 709. [29] Ferrum, 1914, 1, 17.
[30] Comptes rend., 1919, 169, 495; J., 1919, 768A.
[31] Blast Furnace and Steel Plant, 1919, 7, 227 ; J., 1919, 464A.

slag was intermediate between that of dead-burned Canadian magnesite and ordinary calcined dolomite. A pure dolomite resisted air-slaking much less than an impure one containing 6% of silica and 6% of iron and aluminium oxides. Magnesites, low in lime, to which iron oxide had been added before dead-burning showed the highest resistance to corrosion and erosion. These results are quite in conformity with tests made by the present writer on Canadian, Greek, Norwegian, and Styrian magnesites. H. G. Schurecht [32] has made a series of experiments on the dead-burning of dolomite to which various additions had been made. The addition of 10% of coal tar produced, after calcining under strictly reducing conditions, a material which did not disintegrate after standing for two months in water. A mixture containing 30% of iron ore, calcined at cone 18, had a softening point equivalent to cone 31, and offered a high resistance to air slaking. Addition of slags with low silica content gave a product which resisted air-slaking well, but with high silica there was shattering due to the inversion of the calcium orthosilicate formed. It is suggested that for brick-making it is desirable to grind the dolomite with iron oxide before calcination. The increasing production of basic steel in this country renders these results of especial interest, but if additions to the raw dolomite of iron oxide or other material are to be made, considerable modifications of the present practice in dead-burning will be necessary.

J. B. Ferguson [33] in using pure calcined magnesia as an insulating material between the two heaters in a resistance furnace of the cascade type, found that it formed into a dense cake round the inner heater after the furnace had been maintained at 1600°–1700° C. for some hours. This cake consisted of periclase with less than $1\frac{1}{2}$% of forsterite ($2MgO,SiO_2$), and it is suggested that the manufacture of magnesia ware without a binder is possible if the product is fired at a temperature above 1600° C.

[12] *J. Amer. Ceram. Soc..* 1919, **2**, 291 ; *J.*, 1919, 501 A.
[13] *J. Amer. Ceram. Soc.*, 1918, **1**, 439; *J.*, 1919, 106A
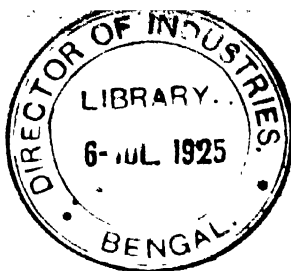
CERAMICS AND BUILDING MATERIALS.

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CERAMICS.

MUCH valuable work in ceramics is in progress in the County Pottery Laboratory, Stoke-on-Trent, under the direction of Dr. J. W. Mellor, and the research into the production of satisfactory hard paste porcelains conducted by Mr. Bernard Moore and Dr. Mellor is likely to have a most important bearing on the future of the ceramic industry of this country. For the last decade this Laboratory has been a great power for good, and nowhere has scientific work been more readily appreciated and had a greater directive influence on industrial progress than in the Potteries.

W. H. Yates and H. Ellam[1] have commenced a study of the bone china body, and in their first paper survey the variations in the colour of bodies compounded with all possible mixtures in 20% variations of the three primary constituents—china clay, bone ash, and Cornish stone- of a bone china body. B. Moore[2] in 1905, in investigating the red coloration of bone china showed the effect of diminishing amounts of alkali or increasing amounts of clay on the coloration of the body, and these authors have amplified the work then commenced The colours of the products varied from a pale cream to yellow and reddish brown, and in one case a deep greenish-blue was obtained Glazes on bodies deficient in stone, and giving greenish-blue and reddish-brown colours, tended to craze, whilst with excess of stone the contraction was high and a tendency to blistering was observed. H B. Cronshaw[3] made a microscopical study of the experimental bodies produced by Yates and Ellam The series of samples showed small angular fragments of quartz and a preponderance of an isotropic and glassy base containing swarms of crystallites, but no minerals having very fully developed crystalline forms. The brown colour of some of the samples was apparently due to the presence of a brownish glass scattered irregularly

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[1] *Trans. Ceram. Soc.*, 1917–18, **17**, 120 ; *J.*, 1918, 208A.
[2] *Trans. Ceram. Soc.*, 1905, **5**, 37.
[3] *Trans. Ceram. Soc.*, 1917–18, **17**, 153 ; *J.*, 1918, 208A.

through the mass. H. J. Plant [4] in treating at length of the milling of potting materials refers to the oft-discussed question of cylinder versus pan grinding. In the opinion of this author, while for such purposes as fritting, cylinder-ground material may be equal to pan-ground, in general the china body cannot profitably be made with materials ground in cylinders. This view received substantial support in the discussion following the reading of this paper. The peculiarity of cylinder-ground material is apparently due to the particles being divided mainly into two groups— fine and coarse- with very little of the intermediate size, whilst in the case of pan-ground material there is a much greater variation in size and a larger proportion of the very fine. In the manufacture of earthenware cylinder-ground materials are successfully used, but in this case the ball clay present gives sufficient plasticity to the body material. E. Watkin [5] examined the effect of pressure on the subsequent contraction, tensile strength, and crazing of tiles. The results indicated that the greater the pressure, the less the contraction. The tensile strength increases and the tendency to crazing decreases with increasing pressure. F. K. Pence [6] in the main confirms these conclusions, but suggests that the use of excessive pressure may cause vitrified tiles to blister or swell. F. W. Walker and E. G. Kerr [7] discussed the effect of a variable percentage of moisture and varying pressures in making dust-pressed tiles of constant body composition, fired at a uniform temperature. The effect of a variation in the moisture contents was found to be of primary importance in all cases.

R. H. Minton [8] considers the "dunting" to which architectural terra-cotta is liable, to be due to the use of grog of an unsuitable character. To avoid this, the use of granulated acid furnace slag as grog is suggested ; abundant supplies of it are available, and it is cheap and light in weight. Any metallic iron in the slag can be removed by a magnetic separator. Bodies made with the slag grog were found to offer greater resistance under the freezing and sodium sulphate tests than ordinary terra-cotta. Only acid slags can be used as the free lime present in basic slags would cause disintegration of the body. E. C. Hill (loc. cit.) considers that the tests applied by Minton are not sufficiently stringent, and that hair cracks can be avoided by a proper control of the composition, size, and proportion of the grog used, and by cooling very slowly below 650° C.

N. B. Davis [9] refers to the successful substitution of selected apatite

[4] *Trans. Ceram. Soc.*, 1917–18, **17**, 123.
[5] *Ibid.*, 1917–18, **17**, 111 ; *J.*, 1918, 208A.
[6] *Trans. Amer. Ceram. Soc.*, 1917, **19**, 94; *J.*, 1918, 508A.
[7] *Ibid.*, 1917, **19**, 409 ; *J.*, 1918, 508A.
[8] *J. Amer. Ceram. Soc.*, 1918, **1**, 185; *J.*, 1919, 14A.
[9] *Trans. Amer. Ceram. Soc.*, 1917, **19**, 125; *J.*, 1918, 509A.

for bone ash in the china body. Commercial precipitated calcium phosphate was found to be much less satisfactory than selected pieces of the mineral phosphate.

Glazes.—C. P. Shah [10] investigated the effect of a glaze containing 0·1 equivalent MgO on various underglaze colours. Chrome and iron browns and greens are completely altered ; crimsons and pinks are destroyed, whilst cobalt blues are unaffected.

H. F. Staley and R. J. Riley [11] consider from the results of experimental work that within fairly wide limits, equal weights of the oxides of potassium, sodium, calcium, magnesium, zinc, lead, and boron have about the same effect on the fusibility of glazes The physico chemical investigation of glazes has been continued by American workers, and the results obtained have been communicated to the American Ceramic Society. H. C. Arnold,[12] in studying the ternary system– willemite, tephroite, soda glass– in its bearing on the production of crystalline glazes, heated to 1175° C. in $3\frac{1}{2}$ hours a series of synthetic mixtures of willemite ($2ZnO,SiO_2$), tephroite ($2MnO.SiO_2$), and a soda glass ($Na_2O,2SiO_2$), and plotted the results on a triangular diagram. The best formation of long acicular crystals of willemite was found in a mixture of equal parts of willemite and soda glass, a larger proportion of willemite producing very small crystals. Less definite crystallisation is produced with manganese than with zinc. Some evidence of immiscible liquids was obtained in various parts of the field investigated. A. S. Watts,[13] in a continuation of his work on Bristol glazes compounded on the eutectic basis, selected three glazes from the eutectic area referred to in his previous paper [14] having the following com position :

				A	B	C
Felspar	.	.	.	60·87	57·07	50·10
Whiting	.	.	.	6·25	5·86	9·01
Zinc oxide	.	.	.	7·76	10·69	9·73
China clay	.	.	.	7·06	8·15	9·07
Ball clay	.	.	.	7·06	8·15	9·07
Flint	.	.	.	11·00	10·08	13·02

When properly ground and mixed these glazes were found to be satisfactory when fired between cones 3 and 14 on a variety of clays. At cones 12 to 14 they were found to be suitable for glazing electrical porcelain. W. G. Whitford [15] has studied the three-component normative systems in raw lead glazes. The further application of the

[10] *Trans. Ceram. Soc.*, 1917–18, **17**, 106 ; *J.*, 1918, 208A.
[11] *Trans. Amer. Ceram. Soc.*, 1917, **19**, 642 ; *J.*, 1918, 511A.
[12] *Trans. Amer. Ceram. Soc.*, 1917, **19**, 674 ; *J.*, 1918, 512A.
[13] *Ibid.*, 1917, **19**, 301 ; *J.*, 1918, 511A.
[14] *Ibid.*, 1916, **18**, 361 ; *J.*, 1917, 716.
[15] *Ibid.*, 1917, **19**, 312 ; *J.*, 1918, 511A.

normative systems of glaze calculation is of interest as when the end members are properly selected ab series of glazes is obtained with physical properties varying in a regular manner. Whitford finds that the glazes in the anorthite series are more refractory than those in the wollastonite and zinc silicate series, and give a larger proportion of matt glazes. This mattness is apparently a function of temperature and composition ; it is determined by the anorthite content and bears no relation to the oxygen ratio. ' In the wollastonite series most of the glazes are bright, and in the zinc silicate series there are mainly bright glazes or enamels, but a few matt and crystalline glazes are formed. F. Zirner [16] considers that the preparation of crystalline glazes for use at temperatures of 940°–960° C. by fusing a mixture of zinc oxide and quartz (corresponding to $ZnO,2SiO_2$) and either grinding the product with lead oxide and calcite or applying it to ware previously coated with a stoneware glaze, is unreliable. A series of glazes was made from mixtures of lead, zinc oxide, calcite, quartz, felspar, kaolin, and rutile, either fritted or used in the raw state. With more than 0·15 equivalent of alumina, matt glazes were produced ; glazes free from alumina gave the best crystals, but were much too fluid. Up to 0·1 equivalent of alumina does not hinder the crystal development and is recommended, as is also a small proportion of alkalis. Good lustre glazes with excellent development of crystals were obtained by addition of molybdic acid. The most satisfactory colours were obtained by the use of copper and cobalt oxides ; with iron, manganese, and nickel oxides the crystal development obtained was poor. The following two glazes gave very satisfactory and uniform results : (a) Red lead, 182 ; calcite, 7 ; quartz, 60 ; felspar, 55 ; rutile, 24 ; molybdic acid, 5½. (b) Red lead, 185 ; zinc oxide, 6½ ; calcite, 5 ; quartz, 75 ; felspar, 22 ; kaolin, 15 ; rutile, 12½ ; molybdic acid, 4. They were used in the raw (unfritted) state, and were fired on a body composed of stoneware clay, 20% ; kaolin, 20% ; quartz, 35% ; felspar, 8% ; chalk, 7% in 20–24 hours in a muffle kiln.

H. Wilson [17] has prepared, for use on terra-cotta, a green glaze of deeper shade than that given by chromium compounds by the addition of 3% of cobalt sulphate and 6% of uranium oxide to a matt glaze of formula 0·261 K_2O, 0·306 CaO, 0·294 ZnO, 0·083 CaO, 0·057 MgO, 0·384 Al_2O_3, 2·08 SiO_2, maturing at cones 3–7 in an ordinary kiln. R. H. Minton suggests that greater regularity can be obtained with a glaze of this type by the addition of a little rutile. H. Wilson [18] and P. G. Larkin [19] describe a method which is in commercial use for the polychrome decoration of terra-cotta with soluble metallic salts.

[16] *Keram. Runds.*, 1919, **27**, 211 ; *J.*, 1919, 682A.
[17] *J. Amer. Ceram. Soc.*, 1918, **1**, 238 ; *J.*, 1919, 15A.
[18] *Ibid.*, 1918, **1**, 353 ; *J.*, 1919, 14A.
[19] *Ibid.*, 1918, **1**, 429 ; *J.*, 1919, 107A.

The salts are applied to the glazed terra-cotta in solution in water, or a mixture of glycerin and alcohol (a suitable dye being added to differentiate the painted areas), and the ware burned to cone 6 7 in ordinary terra-cotta kilns   Larkin considers that the addition of a lead frit to a standard finish engobe greatly improves the colours produced by this method.

H. B. Henderson [20] found about 0·01°/₀ of carbon in salt glazes and considers that it plays an important part in the phenomena of salt glaze reduction.   The present writer, however, agrees with Binns in suggesting that the observed phenomena can be satisfactorily explained by the formation under reducing conditions of ferrous silicate and its subsequent oxidation.   P. Bartel [21] in an investigation of the solubility of lead in fritted glazes found that the resistance of the glaze to 1°/₀ acetic acid was not proportional to the silica content.   It increased up to PbO,2·5SiO₂, but then diminished with more siliceous glazes   Substitution of part of the PbO by soda, potash, lime, baryta, magnesia, or zinc oxide reduced the solubility of the lead and the addition of alumina produced a still further reduction, in several cases a glaze with completely insoluble lead being obtained   R Rieke and W. Steger [22] describe a simple method for the determination of the elasticity of glazes.   The modulus of elasticity of threads or rods drawn from the fused glaze was calculated from (a) the extensibility under tension, (b) the deflection under an increasing load, and (c) the rate of travel of sound through the material.   For a lead stoneware glaze of normal composition, the results obtained were by (a) 6020, (b) 5851, (c) 6175 kilos. per sq. mm.

J Schaefer [23] has successfully used zinc sulphide as an opacifier in sheet iron enamels, but the enamels produced are not so brilliant as those obtained with tin   Enamels in which luminous zinc sulphide has been used have been found to suffer only a very slight loss in luminosity over long periods

J. B. Shaw [24] reduced costs and obtained satisfactory opacity in cast iron enamels by substituting antimony oxide for tin oxide.   The fusibility of the enamel was similar to that of the ordinary tin enamels. It is necessary to pay special attention to proportioning the raw materials, and the batch should be melted under oxidising conditions.

H. F. Staley [25] points out that antimony enamels may contain sodium metantimonate as the opacifier.   In discussing the general practice of the making of cast iron enamels, Staley points out that whereas

[20] J. Amer. Ceram Soc., 1918. 1, 118; J., 1919. 15A.
[21] Sprechsaal. 1918. 51, 25; J.. 1918. 699A.
[22] Keram Runds.. 1918, 27, 193. 203; J., 1919. 634A.
[23] Keram Runds., 1917, 25, 75; J., 1918, 584A.
[24] J. Amer. Ceram. Soc., 1918, 1, 502; J., 1919, 107A.
[25] Ibid., 1918, 1, 702; J., 1919, 176A.

German leadless enamels are usually rich in boric axide, American products of the same type are genera ly high in zinc oxide   The same author [26] defines a satisfactory ground-coat enamel as one which will melt at a dull red heat, will dissolve any oxides or other foreign matter on the surface of the metal, will flow well so as to fill the minute cavities in the surface of the metal and so produce a good bond, and will not blister at enamelling temperatures.   Such ground-coat enamels are generally made by fritting a mixture of quartz, red lead, felspar, borax, and sodium nitrate, cobalt oxide being occasionally added to increase adhesion.   The compositions of five such typical enamels are given. This author in a further paper [27] describes methods for controlling the lustre of enamels   Mixtures containing lead, barium, and zinc oxides give brilliant enamels ; potash gives greater brilliancy than soda, and boric acid than silica ; flint-rich enamels are usually more brilliant than those in which felspar is the refractory base.   E P Poste and B A. Rice [28] discuss the effect of increasing the time of fusion on the properties of enamel frits.   The main effect is to increase the resistance to acid, but the brittleness of the enamel is also increased.

J. N. Collie,[29] in further studying some of the old Chinese glazes, suggests that in the red or reduced copper glaze, the copper is present as infinitely fine particles of metal in the colloidal state diffused through the glaze.   Some support is given to this theory from the fact that the slightest overheating of the red glaze destroys its colour, first rendering it dull brown or opaque, and subsequently almost destroying all colour A cuprous silicate would not be so susceptible to comparatively small changes of temperature as a colloidal solution of the metal.

PORCELAIN.

There has been much progress both in this country and elsewhere in the production of chemical porcelain which will satisfactorily replace the imported ware.   There is still, however, room for improvement in resistance to sudden changes of temperature and in the resistance of the glaze to the action of chemical reagents, before the home production can be considered an absolutely efficient substitute for the " Royal Berlin " porcelain   At the present time the supplies of English chemical porcelain available are only fairly satisfactory, but the indications are that the necessary improvements to render it equal to the best imported material will soon be obtained. G. A Loomis [30] suggests that temperature - porosity and temperature - shrinkage graphs of chemical and other hard porcelains in commercial use should be plotted.

* [26] J. Amer Ceram Soc., 1918, 1, 99; J., 1919, 15A.
[27] Ibid., 1918, 1, 640; J., 1918, 140A.
[28] Ibid., 1918, 1, 221 ; J., 1919, 15A.
[29] Trans. Ceram. Soc., 1917–18, 17, 379.
[30] Trans. Amer. Ceram. Soc., 1917, 19, 636 ; J., 1918, 509A.

A body which remains constant in volume during a long temperature interval, with the porosity remaining at a minimum, will certainly be superior to a body with a shorter range

A. B. Peck [31] discusses the effect on the microstructure of a felspathic porcelain body of variations in the duration and temperature of burning In general it was found that with longer firing the proportion and size of the sillimanite crystals increases, more glass is also produced and the translucency of the porcelain therefore increased

C. C. Lin [32] has conducted experimental work with the object of producing a porcelain body having good working properties in the plastic state and maturing with minimum warping at a temperature sufficiently high to ensure translucency   Twenty-nine porcelains with the following limits of composition were prepared   Canadian felspar 10 20%, Ohio flint 30 45%, a mixture of equal parts of Georgia and Florida kaolin 30 45%, and ball clay 10%   The shrinkage of the different mixtures was irregular but roughly proportional to the clay content   With bodies containing 15 to 20% of felspar, a vesicular structure was developed at cone 13-14 and the shrinkage was less than at cone 10   The most satisfactory bodies were those made from the following mixtures and fired at cone 13-14

Felspar	.	.	.	.	17·5	15·0	12·5
Clay	.	.	.		15·0	52·5	17·5
Flint	.	.	.		37·5	32·5	40·0

Analyses of 59 varieties of Japanese porcelain and of numerous glazes given by V. Kitamura [34] indicate a very wide range of chemical composition   The variations are shown by the following calculated formulæ   for bodies, 0·26 0·57 RO 1 Al₂O₃ 4 68 8·21 SiO₂,   for glazes, 1 RO 0 32 0·99 Al₂O₃ 2 27 8·26 SiO₂

A. V. Bleininger [34] points out that in porcelain fired at cone 10 the amount of undissolved quartz is large and that of sillimanite small, and that consequently such porcelains when subsequently heated are subject to the volume changes due to the inversion of this quartz   In electrical insulators, the permissible proportion of free quartz is low, and the mixture should preferably contain a high proportion of clay. The replacing of quartz by clay or synthetic sillimanite increases the thermal stability of porcelain,   this was especially evident in a particular case with sillimanite prepared by heating to cone 20 a ground mixture of kaolin 258 parts, anhydrous alumina 102 parts, and boric acid 7·2 parts   High mechanical strength can be obtained by replacing part of the sillimanite by calcined zirconia   The electrical

[31] J. Amer. Ceram. Soc., 1919, 2, 175 ; J., 1919, 415a.
[32] Ibid., 1919, 2, 622 ; J., 1919, 767a.
[33] Chem. and Met. Eng., 1919, 21, 183 ; J., 1919, 767a.
[34] J. Amer. Ceram. Soc., 1918, 1, 697 ; J., 1919, 176a.

conductivity of porcelains, as of other vitrified bodies, increases with temperature, but by the elimination of felspar from the body, a porcelain can be made with a resistance of 1 megohm per cm. cube at 800° C. The fact that with high felspar content, polarisation phenomena become more evident indicates that felspar acts as an electrolyte. The use of felspar and quartz should be avoided in making porcelains for high tension use R. G. Allen [35] has measured the electrical resistance between 80° and 300° C. of various samples of porcelain Great differences were observed ; for temperatures below 250 C. the insulation resistance is frequently independent of the voltage. The resistance of Portland china and Royal Worcester chemical porcelain was found to be considerably greater than that of several samples of German porcelain.

Stoneware may perhaps be regarded as a form of porcelain, and should resemble it in its physical and chemical properties H Nielsen and J. R. Garrow [36] suggest that by careful organisation and standardisation in conjunction with adequate research work and plant, the important industry of the manufacture of chemical stoneware may be recovered for this country. There is certainly no valid reason why almost every article could not be standardised in shape and dimensions, and the authors appeal for the adoption of certain standard sizes which they suggest after a series of calculations based on the tensile strength. The ultimate tensile strength of high grade vitreous stoneware varies between 600 and 800 lb. per square inch. It is suggested that the expression " stoneware " should be restricted to dense acid-resisting material used in chemical plant, the term " earthenware " being used for more porous bodies. Probably the first essential is the standardisation of the material and its essential properties for particular purposes rather than the general standardisation of form, but in any case the author's suggestions should receive the serious consideration of all makers and users of this class of material.

KILNS

The high cost of fuel is leading to greatly increased attention to the thermal efficiency of kilns. Attempts are being made to overcome the difficulties which have been met with in the use of continuous tunnel kilns, and their successful solution will lead to very large economies in fuel consumption. A. Bigot [37] describes a tunnel kiln which is completely surrounded by a porous insulating material. It is claimed to have been in successful use for burning a variety of materials at temperatures from 1250° to 1530° C., with a fuel consumption equivalent

[35] Sci. Proc. Roy. Dublin Soc., 1918, 15, 289 ; J., 1919, 140A.
[36] Chem Trade J., 1918, 62, 3, 23, 157, 179, 227 ; J., 1918, 57A, 207A.   Trans. Ceram. Soc 1918, 18, 182 ; J., 1919, 415A.
[37] Trans. Ceram. Soc., 1918, 18, 276 ; J., 1919, 106A.

to from 50 to 105 kilos. per ton, and with an output of from 15 to 25 tons of material per 24 hours. It is considered that narrow tunnels are essential in order to make use of the radiant heat, and that therefore for large outputs a series of tunnels should be used. The fuel consumptions given are exceedingly low and represent a very high thermal efficiency. The cars on which the goods to be fired are carried consist of refractory slabs carried on a series of balls (made from a highly refractory material) contained in a grooved track. A good deal of criticism has been directed against this feature of the design as any failure of the refractory balls due to wear or breakage would cause displacement of the slabs and probable stoppage of the kiln. It appears to be the general opinion of potters that in order to use any type of tunnel kiln with success, standardisation and specialisation of production will be essential. The reorganisation of works will be necessary, it will be necessary to build the factory round the kiln if the maximum advantages and greatest economies are to be obtained

BUILDING MATERIALS

S. Nagaya,[38] in discussing the weathering products of bricks, points out that the efflorescence on bricks is due to the formation of sulphate and carbonate of sodium and sulphate of calcium. The wear of the brick is accelerated by the growth of these crystals, and it is suggested that the bricks should be periodically cleaned by washing with water or dilute hydrochloric acid. Examination of brick clays and shales with regard to their content of soluble salts and sulphur compounds is desirable, and observation should be made of the formation of efflorescences during the drying of moulded bricks

H. Le Chatelier and B. Bogitch[39] have adapted the Brinell ball test to the measurement of the hardness of bricks. A piece of treated lead or copper foil is placed on the brick and the " polish " produced on that portion of the metal surface which has been in contact with the ball facilitates accurate measurement of the diameter of the depression. A series of tests indicated that the foil does not interfere with the size of the depression produced. The ball used is 17·5 mm. in diameter, and is applied for 1 minute under a pressure of 700 kilos. It is claimed that much more concordant results are obtained by this method than by the determination of the crushing strength of the bricks. A test of this type should be useful in controlling the manufacture of bricks as irregularities in manufacture resulting in variations in hardness will be revealed by it.

F. A. Kirkpatrick and W. B. Orange,[40] in investigating the compres

[38] *J. Chem. Ind., Tokyo.* 1917, **20**, 1183; *J.* 1918. 207a
[39] *Comptes rend.*, 1918. **166**, 840; *J.*, 1918. 373a
[40] *J. Amer. Ceram. Soc.*, 1919, **2**, 44, *J.*, 1919. 288a.

sive strength of cement-lime mortars, tested mortars composed of
Portland cement, hydrated lime, and sand of a consistency such that
a 2-in. diam. sphere when dropped from a height of 2 ft. was reduced
to a mass of 1 in. thickness. This is decidedly stiffer than mortars
generally used by masons. Substituting hydrated lime for part of the
sand increased the strength and density of the mortar in a similar
manner as an increase in the, proportion of cement. The relative
strength of these mortars is not indicated by their porosity and water
content, but the compressive strength was found to be in direct pro-
portion to the product of the volume of the cement and the volume of
the total solid constituents per unit volume of mortar. The cubes
used were made by moulding and stored for 28 days before testing.

A. Tomlinson [11] describes the methods in use for the rapid seasoning
of Jarrah wood. Kilns of the compartment-condensing type with
partly forced draught are used, and the humidity is controlled by water-
sprays. The temperature of the air is controlled by the use of steam-
heated radiators and by admitting live steam into the lower part of
drying chamber. Condensed water is used for heating the sprays.
The Jarrah-wood boards are separated by strips 1 2 in. thick, and are
evenly stacked on trucks with a transverse slope of 1 in 7 in order to
facilitate the downward movement of the air during the drying. The
rate of drying is controlled by the daily weighing of specially prepared
test pieces. An excellent account is given of the mechanism of the
seasoning of timber and of the various types of kilns in use for
different woods.

R. Nowotny [12] measured the quantity of mercuric chloride absorbed
by poles of pine and fir trees in a limited time Pine trees were found
to absorb in three days 60% of the quantity absorbed in the usual
treatment, and fir trees 80% in four days. From the known relation
between antiseptic power and the life of preserved wood, the life of
the pine treated in this limited way is estimated at 15 years, and of the
fir at 13 years.

CEMENTS AND CONCRETE.

A general discussion on the setting of cements and plasters was held
by the Faraday Society early in 1918.[13] As pointed out by C. H. Desch
it is now generally agreed that the setting of plaster is caused by the
crystallisation of a super-saturated solution, and the strength of the
plaster depends on the interlocking of these crystals of gypsum. The
presence of salts which increase the solubility of the hemihydrate of
lime (potassium sulphate, for example) accelerates setting ; whilst salts
(such as borax) which diminish the solubility, and colloids, retard

[11] Western Australian Inst. Eng., 14.5.1919; *Engineering*, 1919. **108,** 287.
323 ; *J.,* 1919. 721A.

[12] *Oesterr. Chem. Zeit.,* 1918, **21,** 215 ; *J.,* 1919. 502A.

[13] Faraday Soc, Jan., 1918 ; *J.,* 1918, 32B, 89–91A. See also *Trans. Ceram.
Soc.,* 1918, **18,** 15 ; *J.,* 1919, 417A.

setting. Zinc and magnesium oxychloride cements set by a similar process of crystallisation of an insoluble compound from a solution of the components. Although the conversion of the hemihydrate into gypsum is accompanied by a decrease of 7°/₀ in the volume of the crystals, the mass as a whole expands. Desch regards this expansion as due to the outward thrust of the gypsum crystals during their growth. Overheated (" dead-burnt ") plaster contains a form of anhydrite which sets slowly without expansion The formation of a highly porous plaster is facilitated by fine grinding both before and after burning and by avoiding overburning It is suggested that old plaster moulds might be re-used by fine-grinding, washing to remove soluble salts, burning, and then again fine grinding

There still exists some difference of opinion as to the mechanism of the setting of Portland cement, and the alternative hypotheses were put forward by A A Klein (of the U S Bureau of Standards) and H Le Chatelier. The work of the U S Geophysical Laboratory and the Bureau of Standards supports the hypothesis (originally due to Michaël is) that amorphous and gelatinous products are formed by the hydrolysis, and that the gradual desiccation of these colloidal bodies causes the hardening of the cement On the other hand, Le Chatelier still holds to his original theory that the setting process is essentially identical to that of plaster, the anhydrous cement dissolving to form an aqueous solution super-saturated with respect to the hydrated compounds which crystallise out in a minute interlocked manner and th.s give the product its mechanical strength Desch considers that the difference between the hypotheses is largely one of terminology He points out that the particles of the hydration products are usually of such ultramicroscopic dimensions that the surface forces become comparable with those which bring about the crystalline arrangement. It would, therefore, depend upon the degree of super saturation as to whether the separating particles were colloidal or crystalline He suggests that in such conditions and in view of the work of von Weimarn, showing that the passage from the colloidal to the crystalline condition is continuous, it becomes almost immaterial as to whether the particles resulting from the setting phenomena are described as colloidal or crystalline.

In the work of the Geophysical Laboratory on the ternary system CaO, Al₂O₃, and SiO₂. the chemical constitution of Portland cement clinker has been definitely established. In a well-burned clinker the three compounds, $2CaO,SiO_2$, $3CaO.SiO_2$, and $3CaO.Al_2O_3$ are capable of a stable existence, whilst if the duration and temperature of burning are insufficient $5CaO.3Al_2O_3$ and free CaO are also present.

K Endell,[14] in reviewing the literature on cement published during the last ten years, suggests that as equilibrium is not generally reached

[14] Z. angew. Chem., 1918, 31, 233, 238; J., 1919, 76ᴀ

in the burning of cement clinker, the phases indicated in the triangular diagram may not occur in commercial'cement, and points out that the influence on these phases of magnesia, iron oxide, alkalis, and sulphur trioxide has not yet been investigated, though it is known that quite small proportions of ferrous and manganous oxides prevent "dusting." The results of the microscopical and other experimental work of Ambronn, Kiesermann, Blumenthal, and Schiedler are detailed.   It is shown that after cement and water have been in contact for 2–3 hours, hexagonal plates of calcium aluminate become visible around the cement grains, and fine needles of calcium silicate are also visible.   After 3 4 days the appearance was noted of large hexagonal crystals of calcium hydroxide which in contact with the atmosphere formed spherulites of calcium carbonate, and at the same time a gelatinous calcium silicate is formed.   It is, therefore, considered that the hardening of cement is due to the formation and crystallisation of aluminate and silicate of calcium with a bond of a gelatinous calcium silicate.   J. C. Witt and F. D. Reyes [15] show that when Portland cement is shaken with water free from carbon dioxide, large amounts of lime and relatively small quantities of most of the other oxides are dissolved. Under favourable conditions, the whole of the important compounds present in the cement are rapidly hydrated with formation of calcium hydroxide, the rate and extent of hydration increasing with the ratio of water to cement.   The addition of a larger proportion of water in gauging should therefore facilitate hydration and increase the strength of the cement, but this is more than counterbalanced by leakage of water carrying lime in solution, and the next effect is a reduction in strength of the mixture.   P. H Bates [16] discusses the hydraulic properties of the aluminates of calcium.   A number of mixtures, consisting chiefly of lime and alumina with varying quantities of silica and ferric oxide, were burned at temperatures ranging from 1360° to 1500° C.   The setting time depends on the ratio of lime to alumina.   Several of the mixtures had, after 24 hours, a greater strength than Portland cement after 28 days.   Owing to the high cost of alumina, the commercial possibilities of calcium aluminate cements are not considered promising.

E. Deny and E. H. Lewis [47] described a series of experiments on the effect of the addition of finely ground blast furnace slag to Portland cements.   The quick setting property of cement clinker made from some blast furnace slags can be corrected in this way, and the strength both of this cement and of ordinary Portland cements is improved by such additions

J. C. Witt and F. D. Reyes [48] find that the addition of calcium sulphate to cement to the extent of 1·5–2% SO_3, retarded the setting

[45] *Philippine J. Sci.*, 1918, **13**, 147; *J.*, 1919. 177A.
[46] Faraday Soc., Jan., 1918; *J.*, 1918, 91A.
[47] *J. Amer. Ceram. Soc.*, 1918. **1**, 679; *J.*, 1919, 177A.
[48] *Philippine J. Sci.*, 1917, **12A**, 133; *J.*, 1918, 150A.

time without affecting the tensile strength, but further additions reduced the time of setting and lowered the tensile strength

W. L. Scott [49] describes the making of light-weight concrete for use in reinforced concrete structures. A light aggregate is made by burning clay to 1100° C in 30 hours, the rapid burning causing the clay to swell and form a solid mass of non-porous clinker, which is ground and graded. With this aggregate a concrete may be made weighing about 110 lb. per cub. ft., and with a crushing strength at 28 days of 1000 lb per sq in. As a result of a series of tests L P Hodge [50] considers that where the cost of stone is prohibitive, properly graded well-burned earth (alluvium) may be safely used as an aggregate, and that hard wood may be substituted for iron and steel in fairly large sections when the cost of iron is high

V. Karpen,[51] in a mathematical discussion of the cause of the adhesion of concrete to iron, shows that it is largely due to the contraction of the concrete on setting producing friction between the iron rods and the concrete. A formula for the calculation of this adhesive friction is given

H J M Creighton [52] shows that the deterioration and cracking of reinforced concrete exposed to saline solutions may be due to the action of these solutions on the reinforcement ; the hydrated iron oxide formed having a much larger volume than the original iron, stresses may develop sufficient to crack the strongest concrete A promising protective measure is the coating of the concrete with a film of metal by spraying by the Schoop process

This confirms the suggestion of J L Harrison [53] that the failure of reinforced concrete structures in the Philippines was due to the presence of salt in the concrete mixture or in the water for wetting it down

H Nitzsche [54] discusses the action of calcium aluminium sulphate in destroying concrete Concrete may be rendered resistant to sulphate-containing water by using cements rich in iron oxide or by the use of blast furnace slag cements with low lime content A series of experiments were made in which two Portland cements and one blast-furnace slag cement were immersed in solutions of sodium sulphate and magnesium sulphate of concentrations varying from 0·1% to 20%. The slag cement was found to be much more resistant than Portland cement in both weak and strong solutions of the sulphates

[49] Engineering, 1919, 108, 33 . J , 1919, 636\
[50] Ibid., 1919, 108, 302 ; J , 1919 723\
[51] Comptes rend , 1919, 169, 21. J , 1919, 580\
[52] Faraday Soc , July, 1918 . J , 1918, 468\
[53] J , 1917. 86.
[54] Z. angew. Chem., 1919, 32, 21 ; J., 1919, 178\   Technik. u. Ind., 1919, 81 ; J , 1919. 769\

IRON AND STEEL.

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THE past year has included six months of armistice followed by six months of peace : a time therefore typically of transition, the troublous time in all affairs of life. Technical difficulties have been overshadowed by the continuous disagreements in the settlement of affairs between different groups of human beings connected with the industry. The enormously increased cost of all raw materials and conspicuously that of coal, has made economy in fuel consumption in iron and steel works one of the subjects most thoroughly discussed at public meetings and anxiously debated in private.

There is so much that is uncertain about markets and freedom of commerce that, together with the great need for economy in the expensive item of fuel, there is an increasing tendency to the utilisation of large and self-contained units where the whole series of processes from the extraction of the ore, fuel, and flux from mother earth to the manufacture of the finished product is under one control In Great Britain, where the older plants are already too firmly established to admit of this treatment, combinations of firms are being arranged in order to have a similar effect Several illustrations of this tendency could be given in Britain, but a specially interesting example with some characteristic features is to be found in the Tata Iron and Steel Works at Jamshedpur (Sakchi), Singhbhum, India, which has an additional feature that is believed to be unique, the successful establishment of the heavy steel industry within the tropics. At present the Tata Iron and Steel Company bring their coal from the Jherria Coalfields about 115 miles to the north, their ore from Gurumaishini 40 miles to the south, and their fluxes, refractories, and manganese ore from the east and west. The details of their new scheme are subject to revision as the outlook alters, but as an example of one scheme by Mr. C. P. Perin, consulting engineer to the Company, it is proposed to assemble per annum about 1,130,000 tons of ore, 1,240,000 tons of coal, 386,000 tons of dolomite, partly as a flux for the blast furnaces and partly as a refractory material for the open-hearth, and 72,000 tons of limestone.

Of the 1,240,000 tons of coal about 1,130,000 will be converted into coke in by-product regenerative ovens. The heat units obtainable from the spare coke-oven gas will be used in the most economical manner throughout the works. Already before the writer left India, besides the more customary uses, coke oven gas was conveyed in pipes to the foundry and used to heat the foundry drying stoves. It is intended to extract the benzol from the gases, and as the quantity of tar recovered is likely to be more than the market will absorb, the excess will be used as a fuel for open-hearth work. Of the five blast furnaces, three already in operation, one will be on ferro-manganese when required, smelting the Company's own manganese ores. During the war when ferro-manganese supplies were cut off, the Company made all the ferro-manganese for their own use and exported a considerable quantity to the United Kingdom and to the United States. A proportion of the pig-iron made will be sold, another will be made into cast iron sleepers, pipes, and general castings. The major portion will be converted into steel ingots, partly by the straight basic open hearth and partly by a duplex process. The ingots will be rolled into rails, structural material, merchant bars, plates, and sheets.

Other companies are setting up alongside Tatas. Before the writer left India the Burma Zinc Corporation which will manufacture spelter and supply sulphuric acid to the Tata works for their by-product plant, had cleared their part of the jungle, built their offices and bungalows and started on the foundations of their new plant. Tatas will use part of their own plates and purchase zinc from the Burma Company to make corrugated galvanised steel sheets for which there is a very large demand in India. The Burma Oil Company will import tin from the Straits and make their own paraffin oil cans in another clearing. Messrs. Jessops are already at work in their premises supplying such finished structures as can be moved by rail, so that the scrap made may be returned to the furnaces with a minimum of haulage. Plates for steel sleepers, skelp for welded steel tubes, billets, and wire rods are examples of other products to be made. In order that the Tatas may be able to supply almost any but the finest tool steels, electric furnaces are amongst the proposed equipment.

The Burma Zinc Corporation will manufacture their zinc from sulphide concentrates, and make sulphuric acid as a by-product, of which sufficient will be supplied to the Tata Company for the fixation of ammonia in their by-product plant, and for the remainder a use will most probably be found in the district in a direction in which the writer was experimenting, but which at present is confidential.

The Government of Mysore were about to enter into, and from a press notice have evidently arranged a contract with Tatas to erect and work a charcoal blast furnace plant for them. All that naturally follows the manufacture of charcoal pig is intended to follow.

The whole scheme is outlined as a| interesting example of the trend of companies or combinations of companies being self-contained so as to be able to estimate more closely such items as costs and times of delivery. Other obvious developments are even now under negotiation, all tending in the same direction.

. A similar idea is indicated in a lecture on " Recent iron ore developments in the United Kingdom," by Dr. F. H. Hatch at the Royal School of Mines, on May 27, 1919,[1] in which it was stated that the working of the low-grade Jurassic deposits has been rendered possible by the great extensions to iron and steel works that have been initiated with Government assistance during the war. These works have been planned on the most modern lines, and possess on the same site by-product coke ovens, blast furnaces, steel works, and rolling mills. They are designed for the basic process of steel-making and will be fed with home ores. In choosing the sites for these works regard has been paid to the situation of the raw materials ore, fuel, and flux- required to supply them. On the completion of these extensions there should be no necessity for this country to import a single ton of foreign steel. Before the war something like $2\frac{1}{2}$ million tons of steel, in the form of slabs, blooms, and billets, were imported into this country annually, mainly from Germany. The necessary cheap ore and fuel can only be obtained, in face of great augmented cost of labour and material, by an all-round increase in efficiency, embracing capital, engineering, and labour.

EXTENDED USE OF BASIC STEEL.

Another striking feature is the progressively diverse uses to which basic open-hearth steel is being put, as well as the largely increased output and proportion of basic open-hearth steel in the total output of steel of all kinds. The very large output of high explosive shell would not have been possible along with the other material required had not the result of experiments of experts and manufacturers convinced the authorities of the suitability of this class of steel for the manufacture of high explosive shell. Experience in the war had the effect in many ways of curing us, for a time at any rate, of super-sensitiveness about many things, of which one notable example is the change that it produced in the sulphur and phosphorus contents permitted in steel for high explosive shell which at first had to be made of acid steel to a specification demanding not more than 0.04% each of sulphur and phosphorus It was ultimately [2] found safe to make the shell of basic steel and to raise the sulphur and phosphorus limits to 0.05% in January 1915, 0.06% in October 1915, 0.07% in April 1916, and after experiments on steel containing 0.1% each of sulphur and

[1] J., 1919, 219R.
[2] *Iron and Steel Industry of the United Kingdom Under War Conditions 1914–18*, by F. H. Hatch.

phosphorus, to 0.08%—a change that saved considerable quantities of shell steel from being rejected; 0.08% each of sulphur and phosphorus seems the highest desirable limit, as a higher allowance would not be likely to increase the output of finished product materially.

There was at first a large proportion of rejections on account of surface flaws, and as the writer was in the midst of this work and largely responsible for the scientific side of the Indian production of shell steel bars, he can testify that this to a great extent was another example of super-sensitiveness that was cured by the enemy, a fact which led to the reflection that possibly from even a metallurgical point of view a tonic of this kind had become necessary for the human part of the world.

The period of stress compelled makers also to look at facts squarely. We had been preaching attention to the making of the ingot for over twenty years, and only the manufacturers of special steels and not all of these, paid sufficient attention to the subject but when every bar for shell making had to be broken into shell lengths and the clear fresh fracture examined, there could be no feeling of complacency over steel being free from pipes when they were actually there though hidden, for the fresh fractures exposed the facts to full view. Again, the French practice of having all shell bars pickled was a little revelation of reality to many who, in light of the nicely-finished scale on the outside of bars or billets, felt that their steel had no rokes or similar surface defects. The pickling left the billets naked, with flaws showing black on a white or rather a pale steel grey background a highly educative experience producing in a skilful and determined technician that modesty of outlook that precedes a further and generally a successful onslaught on the problem

Basic Steel for Cutting Tools. What is sometimes called "acid steel made on a basic bottom," a misnomer due to the tendency to claim kindred with more fashionable neighbours, a steel made from pure raw materials and purified to the utmost on a basic hearth, was tried as a substitute for Swedish iron, and either after the old cementation or by carburising in the crucible, made into tool steels which after being tested in the University of Sheffield by Dr Ripper were pronounced to be a success. The use of this substitute was the means of greatly relieving the pressure on imported Swedish materials. We in India had similar problems to meet, only, having no crucible furnaces, had to make our high-carbon steels in the basic open hearth entirely without the after use of the crucible. We were quite proud of our results, but a word of warning is desirable. We have in the past done hundreds of tests on substitutes for the Swedish iron base, and it is most difficult to decide on questions connected with the finer cutting edges. Also, during the stress of war, material was accepted cheerfully that would

not have found a similar market before the war, and might spoil a reputation if presented in the near future.

In 1918, 4,992,106 tons of steel of a total of 9,539,439 tons, or 51%, was made by the acid process and 4,547,333 tons, or 49%, by the basic process. During the last quarter of the year the average weekly output was, acid 85,168, basic 86,122, the first time in the history of British steel making that the output of steel made by the basic open-hearth process exceeded that made by the acid open-hearth. H. Louis [3] mentions that in 1913 7,661,000 tons of steel was made, and in 1918 9,539,000 tons, practically the whole increase being in basic steel from British ores.

Basic Pig-Iron.

Another example of great interest was the modification during the war of the composition of " standard quality " basic pig-iron (silicon not more than 1%, and sulphur not more than 0.05%), as any important increase in the total output was not practicable unless higher limits were conceded.

The problem of increasing the production of home iron-ore is a complex one : not only does it involve the provision of new labour, mechanical appliances, means of transport, etc , but since the ores are in the main phosphoric, it means an extensive rearrangement of plant and the replacement by basic material of the siliceous linings of many steel-furnaces hitherto used for the acid process. Moreover, since the home ores are of low iron-content (averaging 28% iron as against 50% for imported hæmatite), an increased number of blast furnaces are required to produce the same output of pig-iron, and this, in turn, necessitates larger supplies of fuel and limestone More furnaces in blast mean also an additional supply of the specialised labour required to man them ; and the changing over of blast-furnaces and steel-furnaces to basic pig-iron and steel production involves the education of many managements in the technical details of a process to which they are unaccustomed.[1]

The problem of basic-pig iron is a complicated one. The silicon in the pig is converted into silica on the open-hearth, and this must be fed with lime until the slag formed comes up to the high degree of basicity required in the basic process, say under 20% silica. As the silica formed cannot all be brought into contact with added lime, some of it attacks the basic bottom and both on account of the time taken to oxidise the extra silicon and the time taken to repair the cavities made in the bottom of the furnace, a high-silicon pig increases the labour required per ton of steel and decreases the output. Elimination of sulphur is uncertain and troublesome, and the fluorspar used decreases

[3] *J.*, 1919, 205T.   [4] See F. H. Hatch, *J.*, 1919, 219R.

the selling value of the basic slag produced, so sulphur contents must be kept low. In the blast-furnaces the normal conditions tending to low silicon content, tend to high sulphur, and so with a fuel containing about 1% of sulphur it requires a great degree of skill and watchfulness to produce basic pig of " standard quality." Hence in March 1917, after a lively discussion, the steel makers, having regard to the national emergency, agreed to accept a maximum silicon percentage of 1·5, a maximum sulphur percentage of 0·1 and a minimum manganese percentage of 1·25.

Under Indian conditions the sulphur difficulty was not great. There is an abundance of ore rich in iron, about 60%, and nearly free from sulphur, and the fuel contains only about 0·5% of sulphur. Our standard was 0·8–1% silicon, 0·05 sulphur, and 1·1% manganese, which latter with our abundance of manganese ores could have been increased to any reasonable extent, only with our low sulphur fuel a content of 1·1% in the pig was considered sufficient. One of the advantages and disadvantages of the large self contained units is that as your basic pig-iron is your own make and is delivered to you in the molten condition, any not up to the standard is not rejected but must be used under a protest varying in vehemence with the percentage of silicon contained in the pig.

The productions of steel in 1912, 1913, and 1917, compared with 1918 are of interest. In 1912 a total of 6,800,000 tons was made up of 4,310,000 tons acid and 2,450,000 tons basic. In 1913, 7,663,876 tons was made up of 4,800,154 tons acid and 2,863,722 tons basic. In 1917, 9,716,544 tons was made up of 5,673,150 tons acid and 4,043,394 tons basic. During the first half of 1918 the total production was close on a 10,000,000 ton rate, and about the same time the United States had passed the 40,000,000 ton mark.

As in the next great war submarines or similar devices may cut off outside supplies altogether from outlying countries, these countries must arrange meanwhile to be as nearly self-supporting as possible. When we have done our best with basic there may be some of our needs even in times of greatest stress that must be met by acid steel. The coal in India has a low sulphur content, but excepting one small output, a phosphorus content so high that even if the ore contained no phosphorus it would preclude the possibility of making pig iron suitable for the acid steel process.

The present writer has indicated the means * that have been found by experiment and the arrangements made whereby acid steel may be made in India, if the need be great enough, at any time in the future.

The country that can make the best basic steel with regard to price, output, and quality for the work it will be called upon to do and can make the best use of it, has the greatest chance in war. War, so far

* J. Iron and Steel Inst., 1918, i., 451 ; I., 1918, 305A.

as the steel industry is concerned, is an intensified phase of the peace struggle, tonic and educative in its effects. The nation that makes economically basic steel of the most suitable quality for the greatest portion of its demands, assures high reputation and the comparatively unlimited output that under present conditions can only be maintained in basic steel, conserves its acid material for the special purposes for which it is still found necessary or preferable, and thus has the best chance in peace times as in war.

Gradually many of the results of experiments which during the war had to be treated as secret, are being placed on public records. The war produced a curious combination of secrecy and publicity ; on the one hand, results of new work on needs that had developed were kept religiously from the enemy, but spread abroad amongst the Allies ; and on the other, those firms that had attained great success in their special lines not only pooled their information for their mutual benefit, but taught their practice to outside firms for the common good. At a recent informal reunion including several of the manufacturers, one of the most progressive remarked on this subject that now we had divided up our information we must begin again and work even harder and more skilfully than before so as ' to go one better."

NICKEL-CHROMIUM STEELS.

At the September meeting of the Iron and Steel Institute some good papers were given, amongst others two on temper brittleness (*Krupp Krankheit*) especially in nickel-chromium steels.[6] There was an excellent discussion on these papers and some valuable facts were disclosed, especially by J. H. S Dickenson, who has been working on this subject for some years, and has published a valuable paper on nickel-chromium steels.[7] After a brief sketch of the history of special steels, it is stated that the number of special and distinctive steels actually in use is quite limited in number, those of the constructional type (as opposed to tool or cutting steels) being nickel steel, chromium steel, with or without vanadium, the nickel-chromium steels, and, hardly in the same group and only in a special sense constructional steels, the austenitic steels of the 25% nickel, or high manganese, type.

DUTY OF SPECIAL CONSTRUCTIONAL STEELS.

In this connection Dickenson says, in the paper referred to above : " Parts must endure the stresses thrown upon them without fracture and, nearly always, without sensible permanent deformation. The physical properties concerned are elastic limit, ductility, and tough-

[6] F. Rogers, *J.*, 1919, 774A ; R. H. Greaves, M. Fell, and R. A Hadfield, *J.*, 1919, 821A. See also *J.*, 1919, 348B.

[7] *J. West Scotland Iron and Steel Inst.*, 1919, 110.

ness. The last property is usually measured by ascertaining the work of rupture when a notched bar is broken by a blow of adequate force, delivered by a hammer or falling tup or a pendulum." Later he defines toughness in more general terms as the resistance offered to the propagation of a crack.

The significance of these properties is then discussed in detail and the author adds that it is not only possible to get brittleness with soft material of low elastic limit, but also a very considerable amount of toughness with a high elastic limit, and that in securing throughout parts of considerable mass, or of irregular shape, physical properties of a high order and the best possible combination of high elastic limit, toughness, and ductility, alloy steels, and more particularly nickel chromium steels, find their principal application

The author confirms our old observations that this combination can only be obtained when the structure is made up of an exceedingly intimate mixture of ferrite and cementite, but adds that it is fairly easy to understand why this condition leads to higher elastic limit than when the several constituents are separated, and the soft, unstiffened, and unsupported ferrite crystals can give way under stress but less so to explain why it is so advantageous in relation to the notched bar or other toughness-determining test. The reason may be that a crack has so many changes of direction to make in traversing a short distance as compared with the relatively few, long, and straight runs through the crystal gliding planes in a ferrite-pearlite steel.

The structure to aim at in any special structural steel, where high elastic limit is desired, is that produced by the more or less complete suppression of the critical changes when cooling from some suitable temperature, with or without subsequent tempering

A very fine structure, and intimate association of carbides and ferrite, does not necessarily ensure a high elastic limit Certain chromium steels, for example, when slowly cooled through the critical range, give very low yield points, and yet have such very fine structures that high magnifications are necessary properly to see the carbide particles which, however, are then found to be globular Such structures are associated with toughness, but in order to get high elastic limit as well, it seems to be necessary to produce the carbide particles by decomposition of the transition constituent martensite, and not directly from the austenite. It is probable that the carbides then separate as plates, and thus exert their maximum stiffening effect

The intensive hardening of nickel, chromium, and nickel-chromium steels is next considered. All the steels were made to contain as nearly as possible 0·10% Si and 0·25% Mn. The first series had various proportions of chromium and carbon and no nickel , the second was like the first as to the chromium and carbon, but in addition had as nearly as possible 3·75% Ni, and the third series of similar compositions only

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with 5·65% Ni. The whole of the results are most valuable, but probably the most interesting feature of the first series is the critical chromium content varying from about 4·5% Cr with 0·25% C to about 1·5% Cr with 0·8% C. Up to a point depending on the carbon content, the addition of chromium causes a rise, not only in yield point and maximum stress, but also in toughness (as shown by the notched bar test). This effect reaches a maximum at a chromium addition, which is less as the carbon rises, and thereafter the yield and maximum stress decrease without significant further alteration in the impact test results when the carbon is below 0·60%, but with an increase when the carbon is higher. In the second and third series the same type of critical chromium content is shown, which with 3·75% Ni runs from about 3·3% Cr with 0·22% C to about 1·3% Cr with 0·8% C. The other principal point for notice is the considerable raising of the yield point and maximum stress, at all carbon and chromium contents, which follows the addition first of 3·75% and then of 5·65% of nickel. The increased strength produced by 3·75% Ni is not accompanied by any appreciable reduction of toughness in steels having up to about 3% Cr.

It is assumed that a steel which, after cooling, gives a Brinell hardness of over about 115 is effectively hardened through the partial suppression of the critical change, and will, after suitable tempering, give the type of structure desired.

One principal effect of adding nickel to steel containing chromium and carbon (within the limits of composition dealt with) is to make production of martensite much less dependent on the cooling rate than is possible with nickel steels up to 5·65% Ni and about 0·7% C, or with chromium steels containing up to 7% Cr and 0·7% C. In addition, the mechanical tests obtained after hardening and effectively tempering, are improved, up to a point, by increased elastic limit with undiminished toughness. As a consequence, steels containing both nickel and chromium, in suitably adjusted proportions, offer better mechanical properties and may be used for a greater variety of applications, both for large and small work, than either straight nickel or straight chromium steels.

Therein seems to be another feature of the time that has been coming for years, the greatly extended use of nickel-chromium steels. Several years ago A. McWilliam and E. J. Barnes published a series of heat-treatment studies on manganese, chromium, vanadium, and nickel steels of varying carbon content,[8] and in 1910 conducted a series of experiments on the vanadium-chromium, vanadium-nickel, and nickel-chromium series, but some of the results were so extraordinary that it was thought advisable to repeat the whole series afresh for corroboration before publishing them. Many of the results have been used in practice, but

* Iron and Steel Inst., May, 1910 and 1911; J., 1910, 633; 1911, 625.

circumstances prevented the systematic series being repeated   One
of the interesting results of the research was this very improvement
by tempering up to about 300 C. mentioned by the author, and an
example of this was published in one of the papers by McWilliam and
Barnes ; the temperatures varied for different steels between 300° and
400° C.   A similar effect is appearing in work that is being done now
on an altogether different type of material, and that will probably be
published soon.

Temper brittleness   This subject has been so much discussed recently
that it is worth while quoting a portion of Dickenson's opinion on the
subject.

" Nickel-chromium steels, within wide ranges of composition, may
sometimes be made to give very low notched-bar test results, *i.e.*,
become brittle, if slowly cooled through and from a definite range of
temperature below the critical point, after previous hardening   It
is remarkable that this effect, which may be produced or avoided at
will, by varying the cooling rate after tempering, is in some way con-
nected with the melting, casting, or forging of the steel, so that one of
two lots of identical analysis, and made by the same process, may
show marked brittleness, or great toughness, according to whether the
steel is slowly cooled or quenched after tempering at, say, 600 C.,
while the other batch gives good results independently of the cooling
rate.

" This brittleness, which is revealed by the notched bar test only
(tensile and plain bend test giving not the least indication of its presence)
is undoubtedly connected with some alteration of the amorphous inter-
crystalline cement, a characteristic feature being the inter granular
fracture when broken at notches, of temper-brittle steels   The micro-
scope has failed utterly to reveal the least difference in appearance
between two pieces of the same steel which have been hardened alike,
but differently tempered, one to produce brittleness the other toughness,
and this is hardly surprising if indeed the weakness, whatever it is is
confined to the bend, a few molecules thick between the crystalline
grains of sorbomartensite   Marked temper-brittleness only occurs
when oil or other hardening has produced a completely martensitic
structure, with no ferrite meshes between the martensite grains, this
being precisely the condition which gives the best results when temper-
ing is properly carried out, but the significance of this is at present not
very clear.

" Up to the present the principal applications of nickel-chromium
steel have been in connection with war material, including in this term
not merely guns, armour plate, and so on, but ships' crank-shafts, aero
engine parts, etc., and the automobile industry.   It seems very pro-
bable, however, that for more general engineering purposes, where high
stresses have to be met, and especially where these are of the alternating

or fatiguing type, intensively hardening and high elastic limit nickel-chromium steels will tend to displace the softer, and it is important to add, the less tough carbon steel."

The metallurgical world is indebted to the fine spirit that has prompted Mr. William Clark, Director of Messrs. Vickers, Limited, to permit the publication of such valuable results on a subject that is one of the features of the time. An attempt has been made to give the general reader a good idea of the trend of the work, but for those specially interested in it, the paper itself must be studied

DIFFICULTY OF DETERMINING THE RELATIVE TOUGHNESS, BRITTLE-NESS, AND HARDNESS OF STEELS.

The recurrent difficulty of explaining the exact meanings of simple words in common use, mainly no doubt because of the inexactitude of our knowledge, recalls the many meetings that had to be held of a Committee on the Nomenclature of Metallography, and the amount of discussion that took place over defining the meanings of the terms then much in use. For many years there has been much discussion on how to prove whether a steel is brittle or not, on how to ascertain the comparative degrees of brittleness or toughness and even on what test proves brittleness in steel. During the past year the discussion has recurred in a much intensified form. W. H Hatfield in an important paper [a] pays particular attention to the property of brittleness and the attempts to find a test, or series of tests, that will ensure that any steel that is dangerously brittle for the service required of it shall be discovered before being put into use. This paper provoked a most valuable discussion, an indication of the widespread interest in the subject and the difficulty of making clear definitions that will be generally accepted. Dickenson defines toughness as " measured by ascertaining the work of rupture when a notched bar is broken by a blow of adequate force," and its opposite, fragility or brittleness, may be inferred. Hatfield in effect holds that if a steel stands all the tests whilst it is whole and only shows brittleness when it is notched, it has only shown brittleness under one condition out of many possible, and that it should not be called brittle without qualification, but should be referred to as showing notched-bar brittleness. Hatfield holds that if a part is not stressed beyond its elastic range, it must necessarily successfully withstand the stresses with which it has to deal ; that there is a safety range of stress within which any given material may be stressed for an indefinite period ; that there is obviously a minimum range of stress which, over a long period, will produce rupture. However long this latter period may be, it is clear that whilst on more or less empirical calculations the stresses may have been shown not to

exceed the elastic limit of the part under consideration, it is certain that some local piling up of stress must have taken place to produce rupture.

The number of tests to which metals are subjected in a modern works research laboratory may be inferred from the account of the mechanical tests used by Hatfield in the Brown Firth Research Laboratory, of which he is head. " The static tests include tensile, torsion, bend, and Brinell. The dynamic tests include the Izod, Charpy, and Frémont impact tests; the Stanton repeated blow test, the Sankey, Arnold, and Wöhler alternating stress tests, the Shore scleroscope should also be included in this category. There are also the different wear tests such as those devised by Stanton, Santer and others, but those just mentioned represent the ones which the author employs in his different investigatory work." The Izod, Charpy, Frémont, and Stanton tests are all done on notched bars. In investigating failures the examination of samples which have done excellent service is a great assistance despite the adverse opinions of some of the critics. Two main types of failure occur. First, there are those " where the material has rightly been assumed by the engineer to possess strength and freedom from defects, but where the material has failed to live up to reasonable expectations", second, those " where subsequent examination has shown the material reasonably to possess properties which the engineer associated with it, but where failure has obviously been due to insufficient knowledge of to too empirical treatment on the part of the engineer with regard to the stresses with which he had to deal. The author describes in considerable detail his method of investigating failures then discusses the various mechanical tests with examples, giving a valuable table of the results obtained from steels used for different purposes finishing with the mechanical properties of a well known nickel chromium steel, which is employed for a variety of purposes in various heat treated conditions

" Speaking generally, the varying mechanical conditions of such alloy steels produced by successful hardening followed by suitable tempering, are sufficiently indicated by their hardness. Hardness is here spoken of in the sense of resistance to penetration by a steel ball under a static load. When the steel is of low hardness, say, 200 Brinell number, it may reasonably be considered to have a tensile strength of 45 50 tons, accompanied by a high ductility as measured in terms of elongation and reduction of area; a high resistance to rupture under any form of notched-bar impact test, a good value under the Arnold alternating-stress test, but an indifferent value under the standard blow of the Stanton test. Incidentally, it will have a true elastic limit in the neighbourhood of 25 tons. With a Brinell hardness of 275, the tensile strength will be increased to 60 65 tons, with an increase in the maximum stress in torsion. The ductility will show a substantial

decrease, whether judged by the elongation and reduction of area in the tensile or the degree of twist in the torsion test." The energy absorbed by notched-impact test-pieces will be found at a lower value. Incidentally, the elastic limit in tension will be raised to about 40-50 tons, and the resistance under the Stanton test will be very considerably increased. With still greater hardness the same general law is followed, the elastic range being steadily increased   One or two features, however, are distinctly worth noting, namely : (a) The Stanton test attains a maximum of 11,000 blows with a hardness value of about 350, afterwards decreasing   (b) The Arnold test falls to a minimum at about this same value, and then rises again   One further interesting feature is the increase in toughness of the material after passing the hardness number of 450."

The final section of the paper deals with variations in the mechanical properties in steels of the same hardness.   The steel was put into the condition in which it would bear a maximum stress of 60-65 tons per square inch, and in sample " A " notched-bar brittleness was produced by slow cooling from the tempering temperature, whilst in sample " B " notched-bar toughness was produced by quenching from that temperature.   The results are as follows :

				A.	B.
Arnold test	.	.	.	. 230	221
Charpy test	.	.	.	. 16·6 ft. lb	30·4 ft.-lb
Izod test .	.	.	.	. 11 ,, ..	63 ,, ..
Frémont test	.	.	.	. 9 kilos. 12	20 kilos. 60²

Round these and similar results the controversy rages   Hatfield's conclusions are

(1) That all the different forms of tests which have been devised for the mechanical testing of steel bring out some information of interest. The information, however, derived from any particular test needs carefully considering by the engineer in relation to the kind of work which he is calling upon his part to do.

(2) Real brittleness occurs with much less frequency than appears to be generally imagined.   As a result of careful investigation, cases of " apparent " brittleness of the material can be frequently shown to be free from real brittleness.

(3) Notched-bar brittleness must be dissociated from true brittleness, since whilst notched-bar brittleness is always associated with true brittleness, true brittleness does not necessarily accompany notched-bar brittleness.

(4) The tensile test is fundamental, the other forms of mechanical testing being auxiliary and useful in their way for supplementing our knowledge of steels when required for specific purposes

The discussion was remarkable for its interest and value, but the

whole subject is so technical that it is extremely difficult to give a short account of it. Sir Robert Hadfield thought that the Frémont system of testing, which he had used for many years, was the most reliable yet discovered. He felt sure that if the bar without a neck was submitted to a sufficiently high velocity it would show the inherent brittleness shown by the notched-bar test. Dr. Swinden thought that the author had confused two quite distinct features, namely, resistance to fatigue in which the true elastic limit must have a controlling effect, and the low resistance to shock to which the generic term "brittleness" was usually applied.

Mr. J. H. S. Dickenson claimed that perfectly definite determinations of the degree of brittleness were made on ascertaining, by the single blow notched-bar test, the readiness with which a crack could be propagated under fixed conditions which represented the degree of brittleness of the material being tested. Captain E. W. Birch asserted that the only brittleness he knew was notched-bar brittleness.

Mr. H. E. Yerbury said that the car axles of the Sheffield Tramway system had at first been made of mild open hearth steel, they had been satisfactory for about four years, and then fractures occurred at key-ways or close to wheel bosses and about 25% of the axles had broken every year. In some cases, hair fractures had been observed through a magnifying glass, and in other cases a general crystallisation of the metal had appeared to take place. Nickel-chromium steel had then been tried with a slightly larger diameter of axle, and the number of fractures had now been reduced to an average of four per annum.

Mr. Peakman stated that he had never had a failure with turbine discs with manganese nearly up to 2%. Dr. Stanton said that until recently he had always thought that a material which was brittle under the notched-bar test would have the tendency to crack at sharp corners, but recently they had made some experiments, which certainly did not show that effect, and the results were in favour of Dr. Hatfield's argument. Mr. F. W. Harbord said that if engineers were to condemn big forgings on impact tests when the results of all the other tests were satisfactory they would frequently be condemning material suitable in every way for the purpose for which it was required.

Dr. Stead wrote that he was quite in harmony with the author's conclusions, and mentioned that it was well known that after a few years under heavy traffic almost all rails if subjected to the falling weight test when the heads of the rails were put in tension, snapped with a shock of from 8-15 foot-tons; pronounced examples of what the author called apparent brittleness for the same rails, after planing off a layer of 1/16 inch from the surface, stood a shock of 20 foot-tons without breaking. The microscope revealed that the surface layers of the rail had been crushed to a depth of 1/100 to 3/100 of an inch.

Col. H. B. Strang gave some important evidence. He showed photo-

graphs of shells which had been fired through mild steel at an angle,
and in doing the work the points had been very substantially bent.
The Izod impact value was low, only 5 ft.-lb., and the maximum stress
was 60 tons per square inch.   The machining marks were still apparent
on the contour of these points   Each cut formed a minute notch, and
yet these experimental shells had been deformed to the extent shown at
a velocity exceeding 1500 feet per second without fracture.   He
thought that clearly established 'the author's conclusion that notch-
bar brittleness must be dissociated from true brittleness, since it could
hardly be said that these shells were in any sense brittle.   He also
put on record that his firm had, under fire proof tests, obtained abnor-
mally good results with plates which would never have reached the
firing ground if the views held by some enthusiasts of the impact test
had been given the consideration they desired

Dr Hatfield, in the course of his reply, gave the three following defini-
tions : *Real brittleness*   Intrinsic brittleness of the steel. *Apparent
brittleness.*   The kind of brittleness associated with a part which broke
from causes other than intrinsic brittleness of the steel   *Notch brittle-
ness.*   Brittleness which was only to be discovered by means of a
notched-bar test

The serious question behind all this discussion is, that when a test is
placed in specifications, steel must be made to pass that test, even if by
so doing it has to be made of inferior quality to what might be provided
without the test   All these specialist firms can make the steel to pass
the notched-bar shock test, but apparently the author's firm consider
that they can do better by tempering the ardour of the notched-bar
test enthusiasts.   Without pretending to decide such a controversial
subject, it seems to the writer that the realities are not yet sufficiently
clear to found a definition of brittleness on the behaviour of a notched-
bar only, and the discussion has made it plain that for the present the
property should have some distinctive name such as " notched-bar brit-
tleness."   The author's term " apparent brittleness," the brittleness of
the article as distinct from the material, may probably be found useful
as a temporary colloquial term, but one to be discarded as soon as con-
venient, whilst real brittleness both as to its nature and degree still
remains a large field for further thought and experiment.

In a paper dealing with some recent advances in the measurement of
hardness in metals, F C. Thompson [10] brings the almost equally difficult
subject of hardness of metals up to date.

INCREASE IN SYSTEMATIC RESEARCH IN WORKS.

A gratifying characteristic of the present 'time is the amount of
systematic research that is being done in iron and steel works in pre-

paration for the industrial warfare that is bound to follow the military peace. One's own consultation* work during the year has consisted less exclusively in the search after something new or in the elucidation of causes of trouble as in the critical and experimental examination of practice in order to bring each item of it up to the highest profitable standard—a real tuning up. Messrs Bruntons, Wire and Wire Rope Manufacturers, Musselburgh, are the latest to erect and set apart a special laboratory for the purposes of research. Here exhaustive series of systematic researches are being made on the various combinations of heat-treatment and cold-work to produce the best results for the needs of the industries they serve, which include aircraft and bright-drawn materials

New uses for alloy steels and alloys are also the subject of series of experiments, and special attention is being paid to the steel type known as "stainless" in connection with the many new uses to which it is now being put, which will undoubtedly be very considerably added to in the near future now that the embargo on its manufacture has been withdrawn, for during the war chromium was so much in demand for war material that it was deemed well that none should be spared for the manufacture of stainless steels. One result that seems to have been achieved is that stainless knives, which at first lost their edge rather more easily than ordinary carbon steels, can now be relied upon to keep a good cutting edge for a reasonable time and perhaps as well as the best carbon steels They can in any case be re-sharpened to any extent without affecting their stainless property. The probable future developments in the use of this type of steel must be great

The varied applicability of the nickel-chromium steels has already been indicated but Sir Robert Hadfield the inventor of manganese steel which one had come to consider a fixture, has recently patented modifications of his still unique material according to which a tougher steel is produced by increasing the silicon content from 0·6 to 2·5% with 10–17% manganese, and up to 2% carbon [11], a manganese steel of resistant quality with 10–17% manganese 1–4% copper, up to 2% carbon, and 2% silicon, which may be toughened by heating to 1050° C. and quenching in water, has also been patented by the same inventor.[12]

After four years of research the American Malleable Castings Association reports progress of a most practical kind from January 1917, when their castings gave an average strength of 39,882 lb. (18 tons) per square inch with an elongation less than 5%, to March 1919, when the corresponding results were 51,000 lb (22·8 tons) and 12½% elongation.

[11] Eng. Pat. 124867, 1918; *J.*, 1919, 371A.
[12] Eng. Pat. 125157, 1918; *J.*, 1919, 582A.

The position with reference to the employment of electric furnaces in steel smelting is being very carefully re-examined. W. E. Moore, in a paper "The Introduction of the Electric Furnace into Foundry practice,"[13] claims that the electric furnace is the most economical for the production of steel castings, especially from borings and light scrap.

Mr. Cosmo Johns in discussing the solid and liquid states of steel,[14] after describing the surface phenomena of liquid steel as it flows from the launder of an open-hearth furnace, pointed out that the laws governing surface tension applied to samples as usually taken from the bath. He emphasised the necessity of studying heating curves of quenched steels.

The year has been so prolific in good work that the remaining comments must be condensed as much as possible, and will be given shortly under the headings of Ores, Blast furnaces and Cast-Iron, Iron and Steel Manufacture, Studies of the properties and treatment of Iron and Steel.

ORES.

Iron ore. During the war the mineral resources of the United Kingdom have been taken stock of with great thoroughness, and the extended use of home iron ore has already been mentioned.[15]

For the projected State Iron and Steel works in Queensland it is intended to ship ore from New Caledonia to a North Queensland port.[16]

Indian industries during the war - There is extraordinary activity and success in prospecting for iron ore in India[17] One mining engineer informed me that his company had a larger supply of good ore than the United States Steel Corporation.

Manganese ore. It is stated[18] that the deposits of the manganese mines of West Africa should meet most of England's requirements of manganese for many years to come, and that Egyptian and African manganese mines are more favourably situated than Indian ; with the rise in wages the outlook for the Indian mines is serious   It is well to hear of plentiful supplies of manganese ore, as no substitute for manganese in steel-making has yet been found.

In the Report of the Commission to examine into the condition of iron and steel works in Lorraine, etc.,[19] it is stated that manganese was available only in small quantities, and attempts to use calcium carbide as a partial substitute for deoxidising purposes resulted in the production of a high proportion of waste steel ; in fact no satisfactory substitute for manganese was found.

[13] Amer. Electrochem Soc., April, 1919 ; J.,'1919, 420A.
[14] W. Scotland Iron and Steel Inst., Dec., 1918 ; J., 1919, 6R.
[15] J., 1919, 477R.   [16] J., 1919, 416R.   [17] J., 1919, 27R.
[18] J., 1919, 163R, 458R.   [19] J., 1919, 422R,

Tungsten ore.—Pre-war requirements of tungsten ore in the United States were about 2000 tons. The war demand was for 7500 tons (the estimated Chinese output in 1918).[20] The increased demand for United Kingdom may be judged from the fact that by February 1916, 6000 to 7000 tons of high-speed steel per annum was being made, whilst in 1918 the output had risen to 18000 19000 tons per annum, containing some 14 18% tungsten

Molybdenum ores An account by S. J. Johnstone [21] of the molybdenum resources of the Empire is important, as molybdenum is always a possible substitute for tungsten in high speed and other special steels.

Apatite Large deposits of apatite have been found in India, and it has been suggested to use this for enriching Indian basic slag, etc.[22] The writer was working on material from these deposits for Messrs. Tatas during 1918, both from this view and from that of the manufacture of superphosphate. Some portions of the deposit are sufficiently ferruginous to be treated as highly phosphoric ores, which will be of great advantage in the future for the manufacture of highly phosphoric pig-iron for the usual well-known purposes for which it is employed in industry.

BLAST FURNACE AND CAST-IRON.

There is no doubt that the proper manipulation of the slags is one of the great secrets of the successful manufacture of iron and steel A L. Feild [23] deals with slag control in the blast furnace by means of viscosity tables M Neumann [24] discusses the system lime, alumina, silica, in relation to blast furnace slags and cements The important subject of the cleaning of blast furnace gas has been dealt with by W. H. Gellert.[25]

During the war the Tata Iron and Steel Co made sufficient ferro-manganese for their own requirements from their own Indian ores, and exported considerable quantities to United Kingdom and U S A , and in the later stages of the war the Bengal Iron and Steel Co. kept one of their blast furnaces on ferro-manganese the whole time [26] As the writer, whilst metallurgical adviser to the Indian Munitions Board, showed how by taking only one expert from home this could be done successfully and thus help the supply of ferro manganese to the Allies and save much freight, it was gratifying to see that this venture had been the main cause of the good profits of the Bengal Co. in 1918.

[20] *J.,* 1919, 248R, 352R.   [21] *J.,* 1918, 448R.   [22] *J.,* 1919, 228R.
[23] *Chem. and Met. Eng ,* 1918, **18,** 294 ; *J ,* 1918, 735A.
[24] *Stahl u. Eisen,* 1918, **36,** 953 ; *J ,* 1918, 770A.
[25] *Blast Fur. and Steel Plant,* 1919, 7, 334 ; *J.,* 1919, 637A
[26] *J.,* 1919, 27B.

In 1915 shortage of Spanish ore and later of Briey ore necessitated the use of steel turnings at the blast furnaces of an iron-works in the north of France.[27]   At first the use of 10% of the weight of pig produced gave trouble, but later up to 50% was used, and with the complete failure of ironstone, a successful attempt was made to use turnings exclusively.   In 1915 three blast furnaces, two on hæmatite and one on basic pig-iron, worked quite regularly on turnings alone, the monthly consumption exceeding 25,000 tons.   The output of a furnace burning 200 tons of coke per day was 160 tons of pig-iron when using ore and 445 tons when using steel turnings.   So the process might prove to be advantageous even when the cost of the pig is not decreased.   This is a most interesting experience, but in each case the adoption of a similar process would have to be compared with that of the conversion of the steel turnings into steel ingots.

STEEL MANUFACTURE.

Amongst the general survey of processes and materials, refractories have not been neglected.   This will be dealt with fully elsewhere, but the paper on " Basic refractories for open-hearths," by F. S. McDowell and R. M. Howe,[28] records the results of a study of the subject such as many had to make during the war.   In recent years calcined magnesite has gradually been replacing calcined dolomite for basic open-hearths, but since 1914 calcined dolomite had to be largely substituted for magnesite on account of the shortage of the latter; steel-makers are gradually returning to the use of magnesite, which more than compensates in extra wear for its higher price.   In India we were favourably placed in having magnesite from our own mines, although at first there was a difficulty in using it owing to its extraordinary purity.   C. H. and N. D. Ridsdale [29] recommend the use of their steel standards as a help in controlling manufacture to meet the requirements of specifications, and H. Brearley [30] takes the opposite view   Standards are certainly very fashionable and one is able to use them at periods when the type of one's work varies very much.   The standards, where possible, should be of one's own preparation, but even then it is interesting and valuable to check them against some other worker or group of workers such as have produced the Ridsdale standards.   The Iron and Steel Institute is making elaborate arrangements to supply standards for analysis.

In a paper on " The acid hearth and slag,"[31] J. H. Whiteley and A. F. Hallimond describe the microstructure and mineral constitution of acid slags and acid hearths, and B. Yaneske [32] deals with deoxida-

[27] A. Tripier, *Comptes rend Soc. Ind Min*, 1919, **108**, 58; *J.*, 1919, 637A.
[28] *Blast Fur. and Steel Plant*, 1919, **7**, 227; *J.*, 1919, 464A.
[29] *J.*, 1919, 15T.   [30] *J.*, 1919, 97R.
[31] *J. Iron and Steel Inst.*, 1919, **1**, 199; *J.*, 1919, 367A.
[32] *J. Iron and Steel Inst.*, 1919, **1**, 255; *J.*, 1919, 537A.

tion and the influence of lime on equilibrium in the acid open-hearth furnace.

A process that has attracted a considerable amount of attention is represented by patents of C. Dear and the Miris Steel Co.[33] This process starts after the pouring of the ingot. According to the first patent the steel is immersed hot in a solution containing nitric, sulphuric, or sulphurous acid and an ammonium compound, preferably with the addition of ammonia, e.g. 3 cwt. of nitric acid, 2 of sulphuric acid, $2\frac{1}{4}$ of ammonium chloride, and $2\frac{1}{4}$ of strongest liquor ammonia in 1000 qrts. of water. In the second patent, freshly cast ingots, as soon as they can be stripped from the mould, and while the interior is still in a molten condition, are immersed in water or in a solution which will generate hydrogen on the surface of the ingot. The ingot remains submerged sufficiently long to prevent recalescence of the steel when withdrawn. By some it is considered that the hydrogen formed may have a beneficial influence on the steel, but possibly the effect may be partly due to a superior structure of the ingot produced by the rapid cooling. The nature of the differences in properties between Miris and untreated steels and the reasons for the differences are both under investigation

J. C. W. Humfrey, in an interesting paper on macro-etching and macro-printing,[34] details, with very beautifully produced prints as examples, his methods of studying the structure of ingots. The importance of this kind of study lies in the influence that the original structure of the ingot seems to exert through the whole subsequent stages of manufacture. One would like to see a comparative study of examples of Miris and ordinary steel ingots by Humfrey's method

H. F. Bagley[35] has continued his valuable studies of steel manufacture in a paper on "Modern steel metallurgy, calculation and comparison of processes."

J. H. Andrew and G. W. Green,[36] in a paper on the "Manufacture and working of high speed steel," give the practice at the Openshaw works of Sir W. G. Armstrong, Whitworth and Co., Ltd. In "The molecular constitutions of high speed steel and their correlations with lathe efficiencies," by J. O. Arnold and F. Ibbotson,[37] with a note by F. C. Thompson, the more theoretical aspects of the question are given as the results of the culminating experiments of a long series of researches on the carbides in steel. These are followed by a consideration of the correlated influences on the behaviour of the steels in practice.

Another example has been patented[38] of the manufacture of spongy

[33] Eng. Pats. 124463 and 124465, 1916; J., 1919, 371A.
[34] J. Iron and Steel Inst., 1919, 1, 273; J., 1919, 368A.
[35] Ibid., 143; J., 1919, 368A.
[36] Ibid., 305; J., 1919, 368A.   [37] Ibid., 407; J., 1919, 419A.
[38] A. Frankignoul, Eng. Pat. 125194, 1918; J., 1919, 372A.

metal by means of the reducing action of producer gas and its subsequent refining, in this case in an electric furnace.

D. Hanson and J. E. Hurst [39] deal with improvements in the casehardening process. They point out that case-hardening at or above 900° C. tends to the formation of a hyper-eutectoid layer in the case, which is a frequent source of flaking and grinding cracks. The practice of refining $3\frac{1}{2}\%$ nickel case-hardening steel at a temperature lower than the carburising temperature tends to aggravate this trouble. Trouble from this cause may be avoided by (a) quenching the steel from a temperature at which the excess carbide is dissolved, (b) modifying the treatment during carburising in such a manner that a case of practically eutectoid composition is obtained. Of these (b) is preferred.

In a paper before the Manchester Literary and Philosophical Society W. A. Macfadyen [40] shows how worn steel parts may be salved by electro-plating with pure iron, which may then be case-hardened.

G. Taylor [41] gives some points in the manufacture of files that are well worth the attention of those interested.

J. O. Arnold, who has made such a special study of the constitution of high-speed steels, has patented a steel of the following composition : [42] C 0·65, Si 0·35, Mn 0·20, Cr 3·25, V 1·25, Mo 7·50%, which amounts to the substitution of the usual percentage of tungsten by one-half to more than one-third of the percentage of molybdenum.

Several studies of electric welds and welding have been published. E. E. Thum,[43] referring to the welding of tool steel, does not ignore the weaknesses of the process, and shows how they have been overcome. T. T. Heaton [44] considers that further research is needed to establish useful working test methods. J. H. Davies [45] considers that for oxy-acetylene welding pure acetylene and accurate adjustment of the mixed gases to give a neutral atmosphere are essential. In a paper on " Determination of oxygen and nitrogen in electric weld metal," by J. H. Paterson and H. Blair,[46] a general survey of the subject is given with results of series of experiments. Referring to the metal deposited in the weld, the authors state that it has unfortunately been found to be faulty in its mechanical properties, being wanting in toughness and ductility. The percentage of oxygen in the weld varied from 0·13 to 0·37 with one result at 0·753°₀, and of nitrogen 0·08 to 0·14%.

The history and present practice of the American pyrophoric ceriumiron alloy industry is given by A. Hirsch.[47]

[39] *J. Iron and Steel Inst.*, 1919, 1, 383 ; *J.*, 1919, 638A.
[40] *J.*, 1919, 161R.
[41] *J. Iron and Steel Inst.*, 1919, 1, 345.
[42] Eng. Pat. 132082, 1918 ; *J.*, 1919, 826A.
[43] *Chem. and Met. Eng.*, 1918, 19, 301 ; *J.*, 1918, 738A.
[44] Inst. Mech. Eng., Nov., 1918 ; *J.*, 1919, 145A.
[45] Inct. Mech. Eng., Jan., 1919 ; *J.*, 1919, 145A.   [46] *J.*, 1919, 328T
[47] *Chem. and Met. Eng.*, 1918, 19, 510 ; *J.*, 1918, 737A.

TREATMENT AND PROPERTIES OF IRON AND STEEL.

T. Baker summarises his work on the subject of the gases occluded in steel in a paper before the Faraday Society.[48]

R. Ruer[49] deals with the melting and freezing temperatures of the eutectic in iron-carbon alloys and the formation of grey cast-iron. In cast-iron, preferably of about $2\frac{1}{2}\%$ carbon, the existence of two distinct eutectic arrests is shown, the higher the austenite-graphite one at 1153° C. and the lower the austenite-cementite one at 1144° C. The author is of opinion that he has proved by his curves that graphite in grey pig-iron can separate directly from the liquid phase and need not necessarily be the result of the decomposition of pre-existing cementite.

X-rays. A series of papers on the application of X-rays to the testing of metals was read before the Faraday Society.[50] R. A. Hadfield, S. A. Main, and J. Brookbank, testing the absorbing power of steels under X-rays, record the relative absorbing powers of chromium and nickel-chromium steels in comparison with Swedish charcoal iron as a standard. C. F. Jenkin states that the detection of haircracks in aeroplane crank shafts by radiography is not possible. G. Responde found it quite feasible to detect faulty places of $1\frac{1}{2}\%$ of the total thickness of a layer of iron. The method is also very convenient for the examination of reinforced concrete to detect rusting of iron reinforcing bars.

" Flaky " and " woody " steel. In the opinion of F. Giolitti,[51] flaky and woody structures are not formed as cracks in the ingot, but originate as inter-crystalline cracks probably intensified by inclusions and segregations. Hot pouring is recommended. Chromium steel made from pure materials under reducing conditions will never develop flakes either during casting or subsequent forging. In working, the ferrite round an oxidising slag inclusion flattens out into a thin sheet, and if the piece is strained beyond the elastic limit the weaker ferrite is fractured. Heating to 1000° C. for 12–18 hours in a reducing atmosphere will allow equilibrium to be established in defective metal, and a woody or flaky structure may be cured by heat-treatment.

" Flakes " in steel are also considered by H. Styri[52] and by A. W. Lorenz.[53] The former gives a critical review of the literature bearing on oxides and other inclusions in steel segregations, the effect of blow-

[48] *J.*, 1918, 736A.
[49] *Z. angew. Chem.*, 1918, 31, 242; *J.*, 1919, 107A.
[50] *J.*, 1919, 419A.
[51] *Chem. and Met. Eng.*, 1919, 20, 271; *J.*, 1919, 289A.
[52] *Ibid.*, 342, 478; *J.*, 1919, 368A, 683A.
[53] *Ibid.*, 21, 203; *J.*, 1919, 773A.

holes, etc. The flaky fractures investigated are ascribed chiefly to non-metallic inclusions and in a less degree to cracks, blow-holes, and segregations. The latter author records that when using graphite on the ingot moulds 100% good forgings were obtained, but that with tar on the moulds there were several wasters. Whilst the use of tar is not held altogether responsible for the trouble, the author concludes that fibrous structure is often due to the presence of gas cavities, which, during working, become squeezed out into thin streaks without being welded.

Another paper on the same subject is " On the woody structures of fractures of transverse test pieces taken from certain special steels," by J. J. Cohade.[54]

Hardening wire. A method of hardening and tempering steel or other metal wire has been patented [55] according to which the wire is caused to travel under oil. Electric conductors are attached to two rolls and the circuit is completed by the portion of the wire travelling between the two rolls. The heating of the wire is accomplished by this means out of contact with air.

The thermo-electric measurement of the critical ranges of pure iron has been undertaken by G. K Burgess and H. Scott.[56] The Ac3 point of iron of 99-97% purity is given as slightly above 910° C. and Ar3 just below 900° C. as found by thermal, crystallographic, magnetic, electric resistance, and dilatation methods. A2 was indicated by a break at 768° C., but no discontinuity was observed below this temperature. Evidently the authors have resuscitated β-iron notwithstanding its famous " funeral " in another place, for the results are regarded as showing that A2 and A3 are critical points delineating α-, β-, and γ-iron. The results from this source are always reliable and each one can make his own deductions.

L. A. Wild [57] describes a promising method of measuring the magnetic hardness of ferrous metals and shows its utility for carrying out research work on thermal treatment.

A. McCance gives an interesting paper on the carburisation of iron at low temperatures.[58]

In a note on the liquidus in the iron-carbon diagram G. Cesaro [59] details his reasons for considering the formula of the carbide of iron to be Fe_3C and the iron to be present as Fe_2.

[54] Iron and Steel Inst., Sept.; *J.*, 1919, 773A.

[55] H. Alexander, W. T. Vint, and H. Avery, Eng. Pat. 125180, 1918; *J.*, 1919, 371A.

[56] *Bull. Bureau Standards*, 1918, 14, 15, *J.*, 1919, 417A.

[57] Faraday Soc., July 14, 1919; *J.*, 1919, 581A.

[58] *J. Iron and Steel Inst.*, 1919, I, 437; *J.*, 1919, 367A.

[59] *J. Iron and Steel Inst.*, 1919, I, 447; *J.*, 1919, 366A.

Several papers have recently been published on the structure of the iron-carbon-chromium alloys, notably one by T. Murakami.[60]

The influence of the rate of cooling on the hardening of carbon steels has been investigated by A. M. Portevin and M. Garvin.[61] The paper is too long and technical to be efficiently condensed here, but a careful study of it and the discussion which followed should be made by all who are interested in either the theory or the practice of hardening and tempering steels.

[60] *Sci. Rep. Tôhoku Imp. Univ.,* 1918, **7**, 217 ; *J.*, 1919, 257A.
[61] *J. Iron and Steel Inst.,* 1919, **I**, 469 ; *J.*, 1918, 118A.

METALLURGY OF THE NON-FERROUS METALS.

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Although progress in non-ferrous metallurgy reported during the year 1919 shows several points of interest, technical matters have been, perhaps, somewhat overshadowed by economic considerations. The year began with large stocks of metals under the control of the Allied Governments but, under the influence of a greatly increasing demand, accentuated by labour troubles, lack of fuel, and difficulties of transport, during the closing months there was a real scarcity especially of lead, which was soon reflected in the prices quoted on the markets throughout the world.

The formation, under Royal Charter, of an Imperial Mineral Re-Resources Bureau [1] may well have an important influence on the future of the industries of this country and of the Empire. The immediate purposes of the Bureau are, among others, to collect, co-ordinate, and disseminate information as to the resources, production, treatment, consumption and requirements of every mineral and metal. Sub-committees have been formed by the Bureau, upon several of which the Society of Chemical Industry is represented.

The older Mineral Resources Department of the Ministry of Munitions has been disbanded, but apparently the Board of Trade is continuing to some extent its activities, for it is the latter department which has appointed a " Non-Ferrous Mining Commission to investigate and report upon the present condition and economical possibilities of non-ferrous mining and to make recommendations as to such Government action as may be expedient of regard thereto." The industries concerned are also forming bodies and committees, *e.g.*, the Cornish Chamber of Mines (tin, etc.), and the Lead and Zinc Mine Owners' Association. Official inquiry is now proceeding and it will be interesting to see what effort will be made to remove the various anomalies, and reconcile the conflicting interests, now existing.

In connection with the scheme of the Government Department of

Scientific and Industrial Research, the British Non Ferrous Metals Research Association has been formed, with headquarters in Birmingham and with Mr Ernest A Smith as Secretary, for the purpose of promoting research and other scientific work in connection with the study, production, treatment, and utilisation of non ferrous metals and alloys It will be recalled that the Government placed a million sterling at the disposal of the Research Department to enable it to encourage the industries to undertake research and that the scheme provided for a contribution by the Government to the funds of approved Associations, in proportion to the amount raised by the industry itself The Report of the Advisory Council [2] for 1918 19 apart from its general interest, contains few references to non ferrous metallurgy The report of the Tin-Tungsten Research Board is mentioned and also the work of the Copper and Zinc Committee

With regard to progress of a general nature the flotation process of ore concentration continues to show notable advances, and developments of a far reaching character are predicted for the near future, probably in the direction of the flotation of oxidised minerals The Cottrell electrostatic method of fume and dust precipitation, first developed to mitigate objectionable and damaging fumes, continues to find extended applications not only in the recovery of valuable by-products, but as an essential portion of process plants Recent improvements have been described in detail by E E Thum [3]

In his presidential address before the Institution of Mining and Metallurgy, H F Picard [4] remarked that it would probably be conceded that the practice of flotation has brought about greater progress in metallurgy than any other single invention In addition to the increased recoveries of mineral due to the ability of this method to deal effectively with slimes, its adoption has led to a general simplification of concentration procedure, with a corresponding reduction of working costs. A good description of the design and general operation of different types of flotation apparatus has been given by A W Fahrenwald,[5] and it is appropriate to refer here to the paper of far-reaching importance recently read by H L Sulman entitled "A Contribution to the Study of Flotation"[6] dealing with the principles underlying the now recognised practice

The policy of overseas' Governments has been to foster the treatment of ores in the country of origin is far as possible and F A Thomson,[7]

[2] *Report of Advisory Council for Scientific and Industrial Research*, H M. Stationery Office (Cmd 320). 1919.
[3] *Chem. and Met Eng*, 1919, **20**, 59. *J*, 1919, 163a.
[4] *Inst. Min and Met Bull* 176, *J.*, 1919, 207b
[5] *Chem. and Met Eng*, 1918, **19**, 77, 129; *J*, 1919, 44a.
[6] *Inst. Min. and Met. Bull.* 182, *J*, 1919, 450b; 1920, 27a.
[7] *Can. Min. J.*, 1919, **40**, 602.

in his address before the International Mining Convention at Nelson, B.C., taking as his theme the revival of local ore treatment, pointed out that, owing to recent developments in two fields, flotation and hydro-metallurgy, smelting has no longer the supremacy in ore treatment that it formerly enjoyed. The great advantage which lies in mixing ores for smelting does not apply to hydrometallurgy ; in fact, the plant treating ore from one mine is likely to have a simpler problem.

Gold and Silver.

There has been singularly little progress reported relating to the metallurgy of the precious metals, so far as their extraction is concerned. T. B. Crowe's important communication showing the beneficial results obtained by de-aerating cyanide solutions previous to precipitation was referred to in last year's Report. It will be remembered that, arguing that while oxygen is necessary for the dissolution of gold by cyanide, its presence must be undesirable in the reduction process of precipitation, he applied a continuous vacuum to the pregnant solutions during their flow to the precipitation presses. This process has now been installed at some dozen or so mills [8] with satisfactory decreases in the consumption of cyanide and zinc, and the production of a purer bullion. G. T. Hansen [9] found that by heating the pregnant solution to 75°-80° C. to precipitate copper, similar de-aeration was effected, but at a higher cost than by Crowe's method.

The recovery of silver and gold from certain manganiferous ores by hydro-metallurgical methods of treatment presents difficulties which M. H. Caron [10] proposes to overcome by a pre-reduction. In this process the ore is heated to approximately 800° or 900° C. and brought into contact with a reducing gas, such as producer gas, whereby the manganese dioxide is reduced to monoxide and the silver converted into such a form as to be readily recovered by cyanidation. To prevent re-oxidation of the reduced ore, a specially modified, direct-draught furnace has been designed.

The value of flotation methods compared with direct cyanidation for the recovery of gold has been admirably summed up by G. H. Clevenger, [11] who points out that the cyanide process has reached such a high degree of efficiency that extraction cannot be improved upon. As regards cost of treatment, flotation is generally cheaper than cyanidation, but it only produces a concentrate and not bullion, and the cost of marketing the concentrate is often high.

An improvement of the Miller process for refining gold bullion by

[8] *Min. Mag.*, 1918, **19**, 263.   [9] *Chem. and Met. Eng.*, 1918, **19**, 283.

[10] *U.S. Bureau of Mines, 8th Annual Report*, 1919, 79.   Probably refers to Eng. Pat. 101665 15 ; *J.*, 1916, 1161.

[11] *Eng. and Min. J.*, 1918, **105**, 743 : *J.*, 1918, 338A.

chlorine has been described by R R Kahan [12] as introduced by him at the Perth Mint. It consisted of the use of compressed air in addition to chlorine, with the result that cyanide and other bullion high in lead could be more satisfactorily treated G G Griswold [13] has given a good detailed description of the Moebius process for the electrolytic refining of doré bullion as carried out at the Perth Amboy works of the American Smelting and Refining Co The electrolyte is composed of a neutral solution containing 15 20 grms of silver and 30 40 grms. of copper per litre (as nitrates); a current density of 40 amps. per sq. ft. is employed The insoluble residue (gold slime) from the anodes is treated with sulphuric acid to remove silver and copper, and is then melted and cast into anodes for electrolytic refining by the Wohlwill process

The extraction of silver from the Canadian silver cobalt ores forms the subject of an interesting paper by S B Wright [14] of the Deloro Smelting and Refining Company The ore is smelted in a blast furnace, the charge being calculated to furnish speiss and a neutral slag The speiss contains Co 22 25%, Ni 16 18%, As 25%, Fe 18%, S 7%, Cu 1%, and from 1000 to 2000 oz Ag per ton it is first liquated to recover part of the silver then ground, roasted, chloridised washed with water, and treated with cyanide The silver is precipitated from the solution with aluminium dust, the cyanide being almost quantitatively regenerated The liquated and the precipitated metal are melted in an oil-fired furnace which is tilted backwards into blowing position ; the metal after 3 hours' blowing averages from 992 to 995 fine, and is refined by another melting to 996 or better

Sir T K Rose, Chemist to the Royal Mint has carried out [15] an interesting investigation into the losses of gold during melting and finds that true volatilisation (i e vaporisation) of gold is so small as to be negligible at the temperature of industrial furnaces, say 1000°-1300° C, and that the greater part of the net loss represents gold mechanically carried out of the melting furnace in the effluent gases Common experience in mints shows that the gross loss in melting gold-copper coinage alloys is usually 0·2 0·25 per 1000, and after taking account of the amounts recovered, the net loss amounts to 0·1 0·15 per 1000. At the Royal Mint, the net loss over the five years 1909 13 was 0·147 per 1000, equal to an annual average of £9711 The losses at refineries and mills cannot be ascertained accurately but a loss of 0·1 per 1000 would correspond to a total annual loss of £50000, taking the amount

[12] *Inst. Min. and Met. Bull.* 170, *J.*, 1918, 769A.

[13] Amer. Electrochem Soc, Appl, 1919, *J.*, 1919, 181A For further information of these processes in successful operation, see "*Metallurgy of Gold*," Sir T. K. Rose, 1915.

[14] *Canad. Min. Inst. Bull* 80, 1918, 992, *J.*, 1919, 77A.

[15] *Inst. Min. and Met. Bull.* 174; *J.*, 1919, 369A.

of gold melted at the moderate estimate of £500,000,000.   The experiments went to prove that these losses were due to spirting of the gold caused by the disengagement of occluded gases.   Certain gold alloys when molten absorb oxygen, and afterwards, if the atmosphere becomes reducing, will spirt or effervesce until the oxygen is removed   Similarly, Rose found that hydrogen, and in a less degree carbon monoxide, is occluded by such molten alloys, and the metal then spirts in an oxidising atmosphere.   The action is observable in all the alloys of gold with silver and copper ; even parted gold containing 1 part per 1000 of silver is affected, though to a far less degree than coinage alloys.

The volatilisation of silver formed the subject of a paper by F. P. Dewey.[16]   It is invariably stated that little loss of silver occurs in connection with the Parkes process for desilverising base bullion with zinc, and it is true that, with proper care in the maintenance of correct temperatures, it is possible to distil the zinc out of the crusts so that it carries only slight amounts of silver   That such care is not always taken is shown by the analyses of seven samples of Parkes zinc which contained from 28 oz to 604·5 oz. per ton.   Dewey states that the loss is undoubtedly mechanical and has no connection with true volatilisation.   It is caused by excessive ebullition of the zinc in the retort, due to allowing the temperature to rise too high

The properties of standard (sterling) silver, with notes on its manufacture, were given in a paper by E. A. Smith and H Turner.[17]   Silver and copper form an interrupted series of mixed crystals, and segregation of the constituents always occurs during solidification.   The eutectic mixture containing 72% Ag and 28% Cu is the most uniform in composition of all the alloy series.   Standard silver containing 7·5% Cu is invariably richer in silver towards the middle of the cast bar, and a small quantity of pure silver is added in excess to ensure the attainment of the legal standard throughout.

ZINC AND LEAD.

The development of the zinc industry in Great Britain has been disappointing ; the output during the war has seriously decreased, and there appears to be no immediate prospect of much improvement. Completion of the partly erected works at Avonmouth of the National Smelting Company seems to have been postponed and, meanwhile, the Belgian works are gradually becoming productive   Exhortations are still being addressed to the zinc smelters to improve upon their methods and occasionally those intimately interested in the industry retaliate by indicating lines of research which might be usefully followed by metallurgical students and others.

[16] *Eng. and Min. J.*, 1919, **108**, 87 ; *J.*, 1919, 638A.
[17] *Inst. of Metals*, Sept., 1919 ; *J.*, 1919, 823A.

Mechanical blende roasting furnaces, it is generally agreed, have not yet reached the desired state of efficiency, notwithstanding considerable improvements in the existing forms, and the Delplace type of hand-rabbled furnace is still being installed in modern works.

G Rigg [18] desulphurises coarsely granular zinc blende by first subjecting the ore to a partial roast in a multiple-hearth furnace and completing the operation in a blast roaster, e g, a Dwight Lloyd machine, in which air is drawn or forced through the partially roasted ore. The gases from the blast roaster may be passed over the ore in a hearth roaster to increase the sulphur dioxide content. As is well known, the removal of from two-thirds to three quarters of the sulphur in Broken Hill concentrates presents little difficulty, it proceeds rapidly, with small fuel consumption, in furnaces of the reverberatory or muffle type, but the further reduction of the sulphur content is comparatively costly and difficult. Rigg gave last year [19] a detailed description of his method as tentatively carried out at the Port Pirie plant of the Broken Hill Associated Smelters Proprietary. Working on pre-roasted ore containing about 10% of sulphur, one pass over the Dwight Lloyd machine reduced the sulphur content to 1 5%. It was estimated that 75%-80% of the sulphur in the ore could be brought into the form of a gas rich enough in sulphur dioxide to be suitable for the manufacture of sulphuric acid. F W Harbord [20] has patented a method consisting of injecting the finely divided material by means of a blast of air, regulated so as to oxidise the required proportion of sulphur, into an externally-heated vertical or inclined muffle chamber so as to bring it into contact with the incandescent surfaces of the chamber and thus partially to roast the material at the part of the chamber where the injection occurs and to complete the roasting as the material travels down the chamber. C H Fulton [21] suspends finely-divided ore in a slow current of pre-heated air which is caused to pass into a chamber heated above the ignition point of the ore. The desulphurised ore is then separated from the exit gases.

J. C. Moulden, [22] in an informative lecture delivered at the Royal School of Mines, referred to the high cost of recovery of the last 10 or 20% of zinc by distillation and thought that there was distinct promise in the idea, carried out at Bartlesville, Okla, U S A, to distil large tonnages of roasted ore in retorts for a first recovery of 60% of the zinc and to treat the residues in Wetherill grates for the volatilisation and recovery of the balance in the form of zinc oxide for use as pigment. The ultimate yield would be high and the heavier fuel consumption of the final stages of distillation would be avoided as well as increasing the

[18] Eng. Pat. 119223 ; J, 1919, 867A.
[19] Min. Mag., 1918, 18, 285 ; J. 1918. 278B
[20] Eng. Pats. 124265 and 124266, J, 1919, 372A
[21] U.S. Pat. 1273844 ; J., 1918, 660A.   [22] J., 1919, 177B.

capacity and life of the retorts. Pre-reduction of retort charges has also been suggested as advantageous by increasing retort capacity and decreasing the amount of blue powder. P. C. Choate,[23] in a rather pessimistic vein, has given his views concerning the position of the zinc industry in the United States. His remedy for the present high cost of production is the adoption of large vertical retorts and the lime-briquette reduction process, thus avoiding roasting and acid problems and " conserving one-half or more of its labour bills."[24] Within recent years, several inventors have suggested the direct smelting of sulphide ores (chiefly in electric furnaces), using metallic iron or lime as de-sulphurising agents.

Vertical retorts have been patented during the year by several investigators, and J. Armstrong[25] proposes a method for continuous zinc extraction[26] by crushing a previously coked mass of finely-powdered ore and bituminous coal and charging it continuously into vertical tubular retorts formed in three sections, the middle one of which, made of pure silica or corundum, is heated and constitutes the reduction retort. The vapours pass out by a branch through the upper section to a condenser, which may consist of a tank of molten zinc protected from oxidation by a floating hood

The practice at Bartlesville of aiming at a low first recovery of retort zinc and afterwards finishing off on a Wetherill grate has already been referred to At this plant, according to K. Stock,[27] ores and concentrates from the Rocky Mountain region containing various amounts of lead, copper, gold, and silver are smelted. While the retort residues from ores containing little gold and silver are burned for the production of a lead sulphate-zinc oxide fume used as a pigment, the residues higher in gold and silver are clinkered in heaps, after the Petraeus patents,[28] producing a porous blast-furnace material, with no fuel other than the excess carbon remaining after distillation. Residues are selected so that the resulting sinter shall contain as much above 5% of lead as possible (even after a moderate volatilisation loss during the operation of clinkering) 5% being the minimum limit for payment according to smelter schedules. Zinc burns off to a rather greater extent than lead, but even so the finished clinker may run above 10% of zinc at times and be penalised accordingly.

Continued progress is reported in connection with the details of the electrolytic production of zinc, although the output of 1919 from this source has not shown an increase over that of the previous two years.

[23] *Chem. and Met. Eng*, 1919, **20**, 237.
[24] *Met. and Chem. Eng.*, 1918, **19**, 20 ; *J.*, 1918, 471A.
[25] Eng. Pat. 122688 ; *J.*, 1919, 183A.
[26] Cf. the Roitzheim-Remy method ; *J.*, 1916, 846.
[27] *Chem. and Met. Eng.*, 1919, **20**, 525 ; *J.*, 1919, 538A.
[28] A series of U.S. Pats. abstracted in *J.*, 1903, 1002.

The necessity for zinc of high purity for war material undoubtedly gave this method a stimulus and there seems no doubt that, given favourable local conditions and reasonably low electric power costs, the method can hold its own. At Anaconda and Great Falls, where a large amount of experimental work has been done, there was produced a total of 10,000 tons of electrolytic zinc during 1917. The British Empire has not been long in following American enterprise. Before 1916 all zinc ore mined in Canada was sent to the States for smelting and refining. The Consolidated Smelting and Refining Co., operating at Trail, B.C., produced approximately 10,000 tons of electrolytic zinc during 1917, and the establishment of this plant has resulted in the mining and treatment of a much larger tonnage of zinc ores in Canada. The Electrolytic Zinc Co. of Australasia has an extensive local treatment programme embracing, ultimately, the production of zinc oxide, lithopone, and rolled zinc sheets and alloys. The plant is at Risdon, Tasmania, where the present production of electrolytic zinc amounts to about 90 tons weekly, and a further large works is to be erected on the west coast to treat the complex zinc lead ore of the Read Rosebery district.

The fact that success in the electrolytic deposition of zinc depends so largely upon the purity of the electrolyte is reflected in many articles and patents on the subject. D. McIntosh [29] gives the following conditions which must be observed for the best results from sulphate solutions: (1) The solution must be absolutely clear and free from colloids. (2) The iron content should be low, and arsenic, antimony, copper, cobalt, nickel, and, in general, metals more electropositive than zinc, must be absent. (3) The solution should be cold, particularly in tanks containing large amounts of acid. The zinc is deposited in a semi-passive form; but when it begins to dissolve, solution cannot be stopped in any simple way. (4) The zinc concentration should be as high as possible (6-7%) and no attempt should be made to electrolyse solutions containing less than 1·5-2%, of zinc. (5) With the ordinary cascade system the optimum current density is 25-30 amps. per square foot. F. Laist,[30] in order to remove silica in solution and so avoid the loss of zinc and other inconveniences due to gelatinous silica, neutralises the acid and separates the zinc-bearing solution from the insoluble matter. The latter is dehydrated and any zinc present is recovered by a fresh leach. C. A. Hansen [31] states that, of the cumulative impurities, alkali metals and magnesium are unimportant, but even the smallest traces of nickel, cobalt, vanadium, and uranium act injuriously. Cobalt is said to be harmful when present in the electrolyte even in so small a proportion as 0·03 to 100 of zinc. Its

[29] *Trans. Roy. Soc. Can.*, 1917–18, **11**, 113: *J.*, 1919. 42A.
[30] U.S. Pats. 1281031 and 1281632; *J.*, 1919, 19A.
[31] *Trans. Amer. Inst. Min. Eng.*, 1918; *J.*, 1918, 338A.

removal previous to electrolysis is dealt with in patents taken out by G. H. Clevenger [32] and others, among whom may be mentioned the Electrolytic Zinc Co. of Australasia Proprietary who [33] add a soluble manganese compound and precipitate the cobalt and the manganese with lead peroxide or calcium plumbate and sulphuric acid, or [34] by adding a soluble arsenic compound and, subsequently, zinc dust and heating to 60° C.

The most interesting communication during the year relating to thermo-electric methods of zinc distillation is that of C. H. Fulton, who describes [35] a series of experiments carried out in a novel form of resistance furnace. The ore, which may be high or low grade, oxidised or roasted zinc, or complex zinc lead, ore, is finely ground, intimately mixed with finely-ground coke and pitch and, after heating to a temperature of 170–200 C., is moulded under a pressure of 500–1000 lb. per square inch into briquettes measuring 21 in. long by 9¼ in. in diameter. The briquettes thus made are so arranged as to constitute a part of an electric circuit and are heated by an electric current to such a degree that the zinc is distilled. During this operation, the briquettes are covered by a removable retort and the zinc vapour and carbon monoxide are conducted to a condenser in which the zinc is condensed. The briquettes act as continuous resistors, and such an excess of coke is used in their composition that they are indestructible and maintain themselves unaltered in form or volume between the terminal electrodes. A large number of briquettes may be interposed between the terminal electrodes, thus giving a large unit furnace. The briquettes are set up one above the other in a series of columns, all operating in one continuous circuit, upon a fireclay base in which are embedded graphite electrodes for leading in the current. The furnace or retort is dome-shaped and consists of an iron casing lined with refractories and with a detachable connection to the condenser. Blocks of graphite, or blocks made of the briquette material, are used as connectors at the top and bottom of the briquette columns. The whole retort is raised and lowered into position, by overhead gearing, as required.

While either alternating or direct current may be used, the former is the more convenient on account of easy voltage regulation, and the columns of briquettes can be connected to suit any number of phases, giving a quite well-balanced load on each phase. Most of the experiments were carried out with 36 briquettes, and the voltage used was 290 down to 60, three-phase, i.e., 12 briquettes in series. The theoreti-

[32] U.S. Pat. 1283077; J., 1919, 79A.   [33] Eng. Pat. 131898; J., 1919, 827A.
[34] Eng. Pat. 126296; J., 1919, 727A., Eng. Pat. 131702; J., 1919, 827A.
[35] Bull. Amer. Inst. Min and Met Eng., No. 153, Sept., 1919, 2159.   No specific patents are referred to in the paper, but reference to the Journal shows, among others, the following: U.S. Pats. 1242337, 1242339, 1242340, and 1242341; J., 1917, 1240; U.S. Pat. 1213180; J., 1917, 343.

cal power required for an ore containing 60°/₀ Zn with 20°/₀ silicious matter, and briquettes composed of 100 ore, 70 coke, 17 coke pitch, is 1372 kw.-hr (units) per ton of ore (excluding radiation losses), partly made up as follows — 421 kw -hr required to preheat charge to 920 C.; 154, value of CO evolved; 378 heat in briquette residue cooling from 1200° to 250° C. Actual results obtained have varied from 1237 to 3260 kw -hr per ton of ore. The heat required to preheat can be supplied largely by preheating retorts with ordinary fuel or by rapidly transferring a hot retort from a distilled to a fresh charge of briquettes.

It is claimed for the process that it can be applied to any zinc ore, even the so-called complex ores that the zinc is completely distilled and that no blue powder is formed, and that the energy for the distillation is generated within the charge itself which fact, combined with proper heat insulation, will give the minimum power consumption possible. In the larger unit furnace the proposed 12 in — 72 in high briquette, 19 per charge, will distil 8½ tons of roasted concentrate per 24 hours, counting on three distillations of 8 hours each. There is no pottery used in the plant and practically no consumption of fireclay. Labour costs will be low and though a large excess of coke is used in the briquettes (to maintain stability during the distillation) practically only the theoretical amount is used up and the residue may often be used again for making fresh briquettes or as a high ash coke for fuel purposes in power production.

Although the subject of the properties of the manufactured metal is somewhat beyond the scope of this article the work of L. Guillet [36] may be referred to as of interest in view of the suspicion with which zinc containing small percentages of cadmium is regarded. He studied the mechanical properties and microstructure of two series of copper zinc alloys respectively containing 60°/₀ and 70°/₀ Cu and from 0 to 4°/₀ Cd, and finds that cadmium has no effect on the mechanical properties of brasses with 60 or 70°/₀ Cu unless the cadmium content exceeds 1°/₀.

Attention should also be drawn to the excellent work contained in the Fourth Report,[37] by G. D. Bengough and O. F. Hudson to the Corrosion Committee of the Institute of Metals. The report deals (1) with the question of the nature of the actions that take place when metals such as zinc, copper, aluminium and alloys such as 70/30 brass, corrode in neutral or nearly neutral liquids, e g, distilled water and sea water, and (2) the behaviour of condenser tubes in similar liquids and the variations in behaviour in different samples of tubes of nominally the same composition. The third section sets out in some detail a statement of the practical problems of corrosion. This report which is to be regarded as preliminary to a further report upon the study of

[36] Comptes rend, 1918, 166, 735; J., 1918, 338A.
[37] J Inst. Metals, 1919, 21, 37; J., 1919, 5

condenser tubes, might more properly have been referred to under
copper, but 24 pages are devoted to the corrosion of zinc, upon which
very little work has been reported hitherto. Another contribution
of importance to zinc technology, setting forth some of the more scien-
tific aspects, is that of the Research Laboratory [38] of the New Jersey
Zinc Company, Pa., presented by C. H. Mathewson, C. S. Trewin, and
W. B. Finkeldey under the title " Some properties and applications
of rolled zinc strip and drawn zinc rod."

Zinc-Lead. Although, by the immense advances in flotation methods,
much has been done to solve the problem of the treatment of refrac-
tory zinc-lead sulphide ores of the familiar Broken Hill type, and millions
of tons have been treated with the production of smeltable zinc and lead
concentrates, a notable proportion of the metallic values is still lost in
one or other of the products and the ideal method of treatment is, it
appears, yet to be evolved or, at least, proved on the large scale. Pro-
bably there are few, if any, zinc-lead sulphide ores that are not amenable
to flotation with the production of some proportion of smeltable zinc
and lead concentrates, although the percentage of values recovered
varies considerably according to the nature of the ore When, as is
the case with some ores, the minerals, or a proportion of them, exist
in such an extraordinarily fine state of division and so closely inter-
crystallised, the middling or waste products from the use of the best
methods now available may contain a relatively high proportion of the
original metallic values. Even in cases where differential flotation
is not yet practicable, straight flotation is of great value, as it at least
produces a concentrate of metallic sulphides comparatively free from
gangue, thus assisting to make feasible hydro metallurgical or chemical
processes.

Hence, we find mining companies, whose properties contain large
bodies of complex ores, which even now can be profitably worked,
actively engaged in investigating and testing proposed new methods of
treatment which hold out hope of still higher ultimate recoveries. The
recently published annual report [39] of the directors of the Burma Cor-
poration refers to two possible processes, the " Ganelin-Queneau " and
" Elmore " ; it is upon the former that the Company has been experi-
menting during the last two years on an extensive scale. The original
patentee, S. Ganelin,[40] finding that lead sulphide reacted with fused
zinc chloride to form lead chloride and zinc sulphide by simple exchange,
suggested the introduction of lead or lead-zinc-silver sulphides into
molten zinc chloride. A. L. J. Queneau [41] proposes to combine the

[38] *Amer. Inst. Min. and Met. Bull.* 153, Sept., 1919.

[39] *Min. Mag.*, 1919, 21, 258.

[40] Eng. Pat. 26046, 1897 ; *J.*, 1898, 159, and Eng. Pat. 24469, 1899 ; *J*
1900, 1118. ,

[41] Eng. Pat. 116943 ; *J.*, 1918, 518A.

Ganelin process with a flotation process. In his method, crushed mixed sulphide ore or concentrate is treated with excess of molten mixed chlorides of zinc and sodium (60% $ZnCl_2$ and 40% $NaCl$). Metallic zinc is added to the hot mixture to the extent of one-third by weight of the lead present. The resulting mixture is then cast in such a way as to separate the precipitated lead bullion from the rest of the mass, which is leached with water to remove the soluble chlorides and to separate the ore residues and gangue, including a certain proportion of artificial zinc sulphide formed by the reaction of the added zinc. According to the patent specification the leaching is effected under suitable agitation during which a froth is formed on the solution; this froth is collected and removed by any suitable means, such as is employed for the separation of float concentrates. By this separation of the artificially-produced zinc sulphide it is claimed that high-grade zinc product is obtained, suitable for subsequent reduction processes for metallic zinc; such portion of the natural zinc sulphides of the ore as are not floated can be recovered by any of the well known methods of concentration. The flotation of the zinc sulphide may be assisted by the addition of oil, air, or such other materials as are employed in methods of concentrating ores by flotation. F. E. Elmore, whose name was associated with one of the earlier successful methods of oil flotation of metallic sulphides, has patented [12] a process which has received considerable attention in the Press as having been acquired by a Company which was primarily floated for the purpose and whose directors are prominent in mining affairs. According to the patent specifications published at the time of writing, Elmore's process consists essentially of the treatment of zinc-lead ore or concentrate with certain acid agents whereby the lead sulphide is converted into a soluble lead compound while the zinc sulphide remains substantially unattacked. For example, hot concentrated sulphuric acid converts the lead into lead sulphate, which is dissolved by a hot, strong solution of sodium chloride and separated from the unattacked zinc sulphide. Alternatively, the ore is heated with a strong solution of sodium chloride or other suitable halogen salt, to which a sufficient quantity of sulphuric or hydrochloric acid or alkali bisulphate is added. The lead sulphate is smelted with lead sulphide to obtain metallic lead, any chloride produced being first converted into the sulphate.' It is said to be sometimes preferable to treat one portion of the ore with strong and another with weak sulphuric acid, and to pass the sulphur dioxide from the first operation into the second mixture which evolves hydrogen sulphide, which may be used to make lead sulphide from the soluble lead compounds. Elmore also claims the use of strong hydrochloric acid similarly to attack the lead and not the zinc. The lead chloride is dissolved in a hot solution

of lead chloride in water or brine, and separated by crystallisation. The crystals of lead chloride are heated with sulphuric acid, and the hydrochloric acid evolved is used for the treatment of a further quantity of ore.

The Eighth Annual Report (1918) [43] of the Director of the United States Bureau of Mines summarises the Bureau's work in connection with investigations (among others) into the treatment of low-grade lead sulphide and lead-zinc sulphide ores. It is claimed that the problem of treating complex oxidised lead ores by the chloride volatilisation process, referred to in last year's Reports,[44] can be considered as successfully solved and that the results obtained on the volatilisation of lead from sulphide ores have shown the possibility of obtaining, with most of the ores, recoveries of 95-98% of the lead and 75-85% of the silver content. An ore containing more than 10% of sulphur is given a preliminary roast. To the calcine a slight excess of sodium chloride (or preferably a mixture of calcium and sodium chlorides) is added and the whole heated to between 850° and 950° C. The lead and silver are volatilised as chlorides, cooled, and deposited by electrical precipitation. The iron and zinc in the ore are said to remain practically unaffected.

It is seldom that fresh ideas and new methods of treatment do not bring in their wake fresh problems to solve. However successful these chemical processes may prove in opening up the ore, lead sulphate and lead chloride have been found, hitherto, difficult to handle and to smelt, and it will be interesting to follow how these new problems are solved if the processes are ultimately adopted on the large scale. Elmore's proposal to smelt the sulphate with lead sulphide presupposes a sufficient supply of galena or the production of the artificial sulphide. In the U.S. Bureau of Mines experiments, the lead chloride was mixed with lime and coal dust and heated in crucibles; metallic lead and calcium chloride were obtained, but about 15% of the lead was revolatilised even when the operation was carried out in crucibles.

The oxidised zinc-lead ores present a different problem. S. J. Speak [45] describes the metallurgical treatment of the ores of Rhodesia Broken Hill, which is one of the largest deposits known of this kind (probably over one million tons containing 35% mixed metal and practically no gold or silver, although boreholes show the existence of sulphides at depth). The blast furnace treats picked ore high in lead; the slags average about 19% SiO$_2$, 45% FeO, and 18-20% ZnO, and they are liquid even when containing so much as 25% zinc oxide. The chief points making for success in treating a charge so high in zinc are the low blast (about 8 oz.), and the slow rate of smelting (about

[43] J., 1919, 356B.   [44] *Ann. Repts.*, 1918, **3**, 218.
[45] *Min. Mag.*, 1919, **21**, 203.

130 tons of charge per day per furnace). The fuel consumption is not stated. The lead occurs in the ore as carbonate and rarely as sulphate ; the zinc occurs as silicate. The problem of extracting the zinc remains to be decided, but as water power is available, and sulphuric acid can be obtained from the sulphides, some form of electrolytic treatment is foreshadowed.

Electrolytic methods, previously briefly referred to, are, of course, applicable to lead-zinc sulphide ores and, indeed, are more usually applied to that class. The ore is subjected to a sulphatising roast, followed by leaching with sulphuric acid. As an alternative to electro-deposition, which necessitates a high initial outlay for installation, several methods of chemical precipitation of the zinc as oxide have been tried. In one suggested process,[46] sufficient limestone is added to the zinc sulphate solution to precipitate all of the sulphate as calcium sulphate. An excess of sulphur dioxide is then added, which reacts with the zinc to form soluble acid zinc sulphite and sulphuric acid, the latter being precipitated as calcium sulphate by the limestone. The calcium sulphate is removed by filtration and the clear filtrate is heated to remove the excess sulphur dioxide and, at the same time, to form the insoluble normal zinc sulphite, which is then filtered from the treated solution and roasted to zinc oxide with recovery of sulphur dioxide.

Lead. Discussing the subject of losses of metal in smelting for lead, K. Friedrich [47] states that Continental practice tends ever towards poorer charges, down to 10% Pb, in lead blast furnaces. With modern plant and practice, the loss during roasting can be kept down to 1%, of which part is due to mechanical "dusting" and part true volatilisation. The main loss, however, occurs in the final slags, which contain an average of 1.5% Pb, equivalent to 3.5% for a 30% charge and 13.5% for a 10% charge, which latter is becoming more generally practised.

C. E. Barrs [48] has carried out an investigation into the solvent action of concentrated sulphuric acid on commercial sheet lead and finds that, while an increase in purity of the lead renders it more resistant, in most cases of commercial leads the presence of a small amount of copper acted beneficially : the maximum resistance was obtained by the addition of 0·02–0·05% of copper. In the discussion, H. C. Lancaster thought that there was little doubt that the purer the lead the more it would resist the action of acid, and there was equally little doubt that copper acted as a "dope" against certain impurities. Manufacturers were producing to-day sheet lead containing only a small trace of copper which would withstand the action of strong sulphuric acid to a temperature of $310°$–$315°$ C.

[46] U.S. Bureau of Mines, *loc. cit.*
[47] *Metall u Erz*, 1919, 16, 21 ; *J.*, 1919, 259A.   [48] *J.*, 1919, 408T.

COPPER.

In a paper describing the copper industry of the "South West" (Arizona, New Mexico, and Sonora), the biggest copper-producing region in the world, W. Tovote [49] refers to the tendency towards the development of great machine-like organisations utilising lower and lower grade material. Ore containing 1·5% Cu is mined by thousands and thousands of tons a day, and while fifteen years ago smelting of less than 9% ore was considered impossible, 4% and even 3% straight-smelting ores yield good profits, while Bisbee holds the record in smelting ore so low as 2% Cu. The daily output of mines ranges from several hundreds of tons up to the wonderfully organised Inspiration Mine with its record of 21,000 tons of ore a day.

Referring to the formerly much debated question concerning the respective merits of blast and reverberatory furnaces (except in particular cases), O. E. Jager [50] says that the trend of opinion for several years has been going steadily in favour of the reverberatory, and he recapitulates the chief disadvantages urged against the two types. At Anaconda, where the normal monthly production of copper is about 11,500 tons, practically all the ore smelting is done in reverberatories which, in spite of all the extra operations, is cheaper than blast-furnace smelting. Increased efficiency is obtained by using pulverised coal as fuel.

The cost of coke is a serious item in blast-furnace practice. At the Tennessee Copper Co.'s smelter at Copperhill and at the International Nickel Co.'s smelter in Ontario, satisfactory results have been obtained experimentally by introducing pulverised coal with the blast at the tuyères.[51] In the former works, on a high-sulphur copper ore, the pulverised coal amounted to 3·8% of the charge, as against 5·7% of coke used on the other furnaces; at Copper Cliff, operating on a copper-nickel ore, the coke was partly substituted only, but experiments are being continued. It is also announced that the blast furnaces at Cerro de Pasco copper mines in Peru are to be modified for the use of pulverised coal and that furnaces are to be built on the new system. This important subject has been very fully dealt with in a paper by E. P. Mathewson and W. L. Wotherspoon,[52] who give details of the plant and experiments carried out at Copper Cliff, with probable cost of operating.

The forms in which copper occurs in smeltery slags has been investigated from the microscopical and chemical point of view by C. G. Maier and G. D. van Arsdale.[53] The conclusion is arrived at that, in the samples examined (which were representative of present practice of

[49] *Min. Mag.*, 1919, **20**, 339.   [50] *Min. and Sci. Press*, 1919, **118**, 843.
[51] T. W. Cavers, U.S. Pat. 1259467, *J.*, 1918, 309A.
[52] *Can. Min. Inst. Bull.*, July, 1919; *Min. Mag.*, 1919, **21**, 139.
[53] *Eng. and Min. J.*, 1919, **107**, 815.

matte smelting at the Phelps-Dodge properties), little or no oxide copper is present in either blast-furnace, reverberatory, or converter slags, and that the copper exists in two physical forms, chemically similar : (1) Dissolved copper sulphide, in blast-furnace and reverberatory slags, usually about 0·15% Cu , in converter or mixed slags up to 0·5% Cu. (2) Mechanically suspended particles of sulphide copper varying in composition from matte to $Cu_2S + xCu$ and, in amount, equal to total copper less dissolved copper. The probable main cause of the retention of mechanically suspended particles, apart from insufficient settling and viscosity, is the attachment of gas bubbles, probably due to the action of ferric iron in the slag or iron sulphide in the matte. The dissolved copper sulphide content acts like a saturated solution in respect to fusion with such additional agents as pyrites, iron sulphide, and calcium sulphide.

Little is heard now of electrothermal processes in connection with copper. According to an abstract of a German patent applied for by a Norwegian Company,[54] it is proposed to heat copper bearing pyrites with silicon to about 1500 C, out of contact with air, preferably in an electric furnace. Ferro-silicon is said to be formed, the sulphur distilled, and the copper concentrated in a matte. From the scanty particulars so far available, this does not appear to be a very economical proposal.

Leaching processes provide a mass of reading matter in the technical press, and keen interest continues to be shown generally in connection with the treatment of low-grade oxidised copper ores which exist in enormous quantities in deposits situated in many parts of the world. A great number of patents have been applied for, but many appear to have no particular novelty. Most attention is paid to the conditions necessary for the sulphuric acid leaching of such ores, which process is also applied, in some instances, to roasted sulphide ores and to flotation concentrates. Of course careful roasting will alone convert a large, perhaps the major, proportion of the sulphide copper into water-soluble copper sulphate. P. R. Middleton [55] states that during roasting, chalcopyrite is converted to cuprous sulphide and ferrous and copper sulphates below 550 C, below 650 C cuprous sulphide is converted into copper oxide. The use of Dorr agitators and thickeners for the leaching process is increasing and the copper-bearing solution is treated either with scrap iron or by electrolysis. N. Evans [56] proposes to treat ore containing oxidised copper minerals with an aqueous solution of nitre-cake in place of sulphuric acid. A. W. Hahn [57] proposes passing the acid leaching solution through a series of tanks con-

[54] Ger. Pat. 310526 , J., 1919, 323s
[55] Aus. Chem. Eng. and Min. Rec., 1919, 11, 133 ; J., 1919, 389A.
[56] U.S. Pat. 1297670   J., 1919, 374A.
[57] U.S. Pat. 1282415   J., 1919, 45A.

taining ore until it becomes neutral ; it is then passed through a fresh charge of ore whereby ferric iron is precipitated. The solution thus freed from ferric iron is acidified, electrolysed, and returned to the tanks. At the property of the New Cornelia Copper Co., Arizona.[58] a daily output of about 5000 tons of oxidised (carbonate) copper ore containing about $1\frac{1}{2}\%$ Cu was treated by leaching with sulphuric acid. The solution from the leaching tanks, containing the dissolved copper, also contains a considerable amount of ferric iron, to reduce which the solution is passed through towers where it comes into contact with sulphurous gases before going to the electrolytic tanks. The leached residues contain about 0.3% Cu.

The leaching of copper ores with ammonia and ammonium carbonate was referred to in last year's Report. L. Eddy,[59] describes the process as carried out at Kennecott, Alaska, on tailings from a wet concentration mill. The ore as mined contains chalcocite (Cu_2S), covellite (CuS), and malachite in a limestone gangue, the treatment of which, by wet dressing, results in a good recovery of the heavy sulphides, but a loss into the tailing of 10% of the copper present as malachite. Ammonia recovers no gold or silver values, and no copper sulphides unless roasting is first resorted to.[60] Before leaching with ammonia, the mill tailing is de-slimed as the presence of material less than 200-mesh in size causes the ore to set in the tanks. Ammonia solution is admitted through the bottom of the leaching tank, and is allowed to remain in contact with the ore for twelve hours without agitation. The resulting dark blue solution is heated, yielding ammonia vapour and carbon dioxide, and a heavy black deposit consisting chiefly of cupric oxide. The initial difficulties, mainly mechanical, in dealing with the ammonia-copper solution have been apparently overcome and the plant has seen two years' continuous working, averaging 450 tons of mill tailing per 24 hours. The oxidised copper content of the ore leached was 0.85% Cu, and the residues after treatment contained 0.17%. The recovery amounted to 13.3 lb. Cu per ton of tailing treated, and the total cost was less than \$1 per ton, including the loss of 0.51 lb. of NH_3, but excluding overhead charges and cost of mining and crushing the ore, tailing disposal, etc., which are properly charged, in this case to the main plant, as it would have to bear this expense if the tailing was not treated.

In Arizona there is now being erected a 100-ton plant for testing on

[58] Eng. and Min. J., 1919, 107, 398.

[59] Chem. and Met. Eng., 1919, 20, 328 ; J., 1919, 369A.

[60] In H. O. Hofman's "Metallurgy of Copper," 1914, it is stated that cuprous sulphide is attacked by ammonia solution charged with some ammonium salt, but the action is slow unless an oxidising agent (air, manganese dioxide, bleaching powder) is present. This was confirmed by the present writer during the course of some small scale experiments carried out on sulphide copper ores.

a semi-commercial scale a process worked out by the U.S. Bureau of Mines Experimental Station [61] The apparatus devised for treating the low-grade " porphyry " ores, containing oxides, carbonates, and silicates of copper, in addition to some sulphide copper, comprises a rotating drum in which the ore pulp of proper consistency is met by a countercurrent of heated air carrying 0·5 0 6%, of SO_2 under slight pressure. The advantages of the apparatus are stated to be economical use of sulphur dioxide, rapidity and thoroughness of solution, and economy of construction and operation The oxidised copper minerals are dissolved and any sulphides present are left in good condition for flotation. Further details are not given in the Bureau of Mines Report, and it is not apparent how this differs from the Neill process which depended upon a similar use of sulphur dioxide and the subsequent precipitation of the copper by heating the solution N. C Christensen [62] lixiviates with a concentrated solution of sulphur dioxide, made by first bringing the solution into contact with gases relatively poor in sulphur dioxide and then successively in separate absorbers with gases relatively stronger in sulphur dioxide In further patents [63] Christensen proposes to add metallic copper to the solution, which is boiled to expel the excess of sulphur dioxide, when a precipitate of cupro-cupric sulphite separates Alternatively ore is treated to convert the copper into cupro cupric sulphite which is separated from the remainder of the ore by a flotation process

Both the ammonia and sulphur dioxide processes have the advantage that no metallic iron or electrolysis is required for the recovery of the copper from solution and. moreover, it would be probably of a greater purity than ordinary cement copper.

Recent improvements in the Longmaid-Henderson chloridising-roasting process for the extraction of copper and precious metals from burnt pyrites have been described by P. Klason [64] and D. W. Jones.[65] The Ramen-Beskow furnace is chiefly used in this country, four of the most recent type treating about 1300 tons weekly. Klason enters very fully into the chemical reactions taking place in the furnace, and also forecasts the future economic extraction of other metallic constituents of pyrites, such as zinc, nickel, and cobalt besides the copper and silver now recovered. Claudet's iodide method, is employed for the recovery of the silver, and it may be recalled that, in describing this process in a paper read before the Society some few years back.[66] the late A. F. Claudet stated that in years gone by, when silver was 5s. per oz., a profit was made with an ore containing only 1–1½ oz. of silver per ton and 3 grains of gold In this connection Jones states

[61] *Loc. cit.*   [62] U.S. Pat. 1278854 . *J.*, 1918, 772A.
[63] U.S. Pats. 1316351 and 1316352; *J.*, 1919, 828A.
[64] *Min Mag* , 1918, **19**, 287, 301
[65] *J.*, 1919, 365T, and *Chem. Tr. J.*. 1918, **63**, 479   [66] *J.*, 1919, 1422.

that a recovery of 96% of the silver is effected with a loss of from 15 to 33% iodine.

S. Skowronski and K. W. McComas read a paper before the American Institute of Metals [67] on the volatilisation of cuprous chloride which is of importance in connection with the melting of copper cathodes, since any copper-leaching process giving chlorides either from the ore or solvent will electrolytically deposit cuprous chloride on the cathodes. Experimentally, a small amount of copper containing various amounts of chlorides was melted and the volatilised copper chloride determined. From the results obtained, it is considered that, under present refinery practice, all cuprous chloride in cathodes will be lost by volatilisation.

ALUMINIUM.

While much attention is being given at the present time to the properties and uses of aluminium and its alloys and many interesting papers have been written in this connection during the year,[68] very little technical information concerning the production of the metal has been published. Water power is being further utilised in Norway for the manufacture of aluminium and a works is said to have been completed at Hoyanger, in association with French interests, for a first annual production of 7000 tons.

The deposits and production of bauxite are receiving much attention from Government departments and individuals in many parts of the world, and during the year a great number of patents have been applied for in connection with the utilisation of low-grade silicious and ferruginous bauxites and other aluminous rocks as sources of aluminium. A process which is said to be experimented upon at the present time in Norway has been patented by O. Ravner and V. M. Goldschmidt,[69] who propose to employ plagioclase rocks of the labradorite-anorthite series which produce aluminium chloride when mixed with carbon and heated between 600° and 1000° C. in a current of chlorine or hydrochloric acid, or aluminium oxide and sodium and calcium nitrates when heated to 300° 600° C. in a current of nitrogen oxides and steam. In the latter case, the mixed salts are evaporated and heated to the temperature required for the decomposition of the aluminium nitrate alone. The evolved nitric acid is collected, and the sodium and calcium nitrates recovered from the residues for use in agriculture. It is said that this process is now being tried out at an experimental works near Christiania.

Cast aluminium, according to R. J. Anderson,[70] readily forms den-

[67] *Chem. and Met. Eng.*, 1919, **20**, 211.
[68] Reference may be made particularly to bulletins issued by the U.S. Bureau of Standards and to the papers published in the Journal of the Institute of Metals.
[69] Eng. Pats. 126678 and 113278; *J.*, 1919, 133A. See also *Nature*, 1919, **104**, 160.   [70] *J. Franklin Inst.*, 1919, **187**, 1; *J.*, 1919, 289A.

dritic crystals on cooling, but the commercial metal is rarely of a high state of purity as compared with the purity of commercial copper, zinc, and tin. Metal containing 0·15% Cu, 0·30% Fe, 0·30% Si, and 99·15% Al (by difference) represents a fairly good commercial product, and the influence of iron and silicon, although not thoroughly understood, is important, both in commercial aluminium and in its alloys. In a further paper, Anderson[71] stated that aluminium ingot is usually divided into two grades, containing respectively 99% and 98·99% Al, though the chemical composition is not now regarded as a complete criterion of quality owing to the widely different physical properties (e.g. toughness) shown by different ingots of similar composition

· NICKEL AND COBALT

Following the armistice, the International Nickel Company closed its Crean Hill Mine and the Mond Nickel Company curtailed operations at its smelters and mines in Ontario and also at its refinery plant at Clydach, South Wales More recent news shows that the industry in Canada is recovering from the depression the International Nickel Company increasing the number of men employed earlier in the year and the Mond Company resuming shipments of matte to their refinery in Wales The new works of the British America Nickel Corporation, which has adopted the Hybinette electrolytic process for refining the matte, is nearing completion and is expected to commence smelting during the spring

The Report of the Royal Ontario Nickel Commission (1917) referred to experiments carried out by Prof G A Guess in the electrolytic refining of the Sudbury bessemer matte Guess has published further work[72] on a process tested on a laboratory scale Anodes of crude nickel, containing copper and iron, are suspended in a bath of nickel sulphate to which finely-divided calcite is added periodically, the cathodes (lead or aluminium) are enclosed in a bag of light canvas, mounted on a wooden frame. The copper is precipitated as a basic double sulphate, $2CuO,2NiO,SO_3$, which settles in the form of mud, which is fused with silica in graphite pots to a matte containing Ni 36·1, Cu 37·8, and S 19·5%. The matte may be roasted, then reduced to metal and cast into anodes, from which the copper can be recovered electrolytically. The nickel anodes are produced by roasting copper-nickel matte, leaching the calcine with dilute sulphuric acid to extract the bulk of the copper, fusing the dried residue with charcoal, and casting the crude metal. The nickel deposited on the cathode is said to contain usually less than 0·001% of copper.

[71] *Chem. and Met. Eng.*, 1919, 21, 229; *J.*, 1919, 776A.
[72] Amer. Electrochem. Soc., Apr. 1919; *J.*, 1919, 182A. See also U.S. Pat. 1251511; *J.*, 1918, 155A.

J. Dhavernas [73] reduces the roasted copper-nickel matte and dissolves
the copper with neutral or slightly acid copper solution. The solution
is treated with metallic nickel to precipitate traces of copper, and the
solution of nickel salts drawn off. B. Mohr and C. Heberlein [74] roast
finely-ground copper-nickel matte to oxide, reduce in an atmosphere of
water gas, and leach with 10% sulphuric acid at 80°-90° C. A deposit
of nickel is obtained by electrolysing the dilute solution of nickel
sulphate so produced, and the resulting acid solution is used for leach-
ing a fresh quantity of the reduced matte. The residues containing
copper and precious metals are cast into anodes to be refined electro-
lytically.

Low-grade nickel ores have been investigated by C. W. Davis,[75]
who expresses the opinion that a silicate ore of the North Carolina type,
containing nickel oxide 1·2% (-0·97% Ni), silica and insoluble 56·5%,
iron oxide 22%, alumina 4·1%, magnesia 7·2%, might be economically
worked by a process involving the reduction by producer gas at
1000° C. and dissolution of the finely-divided metallic nickel with
dilute sulphuric acid. There must be, however, but little iron present.
H. W. C. Annable [76] suggests heating silicate ores in presence of moist
hydrogen sulphide or other sulphur-yielding material, such as pyrites,
in presence of steam, preferably with the addition of a small quantity
of sodium or potassium chloride to the charge. Nickel sulphide is
formed which may be oxidised to sulphate, any oxysulphate being
dissolved by means of hydrochloric acid obtained from the furnace
gases. In a further patent [77] Annable describes the treatment of sul-
phide ore or matte at 800-1000° C in a non-oxidising atmosphere,
and the conversion of all the nickel into sulphide form. The mass
is oxidised in contact with air at a temperature sufficiently high (500°-
600° C.) to decompose iron or copper sulphates, but below the decom-
position temperature of nickel sulphate. The latter is leached out with
water.

The manufacture of " Nicu " steel was described by G. M. Colvo-
coresses,[78] who revives the idea of the direct production of an alloy
pig-iron from Sudbury ores which is subsequently refined to produce
nickel-copper (Nicu) steel.

The uses and production of the cobalt-chromium-tungsten alloy
known as " Stellite " have been described by S. B. Wright.[79] In addition
to its uses for high speed tools, the alloy is employed in the manu-
facture of motor cars and a malleable form, of modified composition,

[73] U.S. Pat. 1273465; J., 1918, 591A.
[74] Eng. Pat. 125642; J., 1919, 422A.
[75] J. Ind. Eng. Chem., 1919, 11, 644; J., 1919, 585A.
[76] Eng. Pat. 125119, J., 1919, 373A.
[77] Eng. Pat. 129667; J., 1919, 685A.
[78] Trans. Can. Min. Inst., 1918, 21, 48; J., 1919, 326A.
[79] Trans. Can. Min. Inst., 1918, 21, 272; J., 1919, 326A.

is also made for various purposes requiring a metal resistant to corrosion due to atmospheric and other influences

TIN AND SOME MINOR METALS

The Report of the Tin and Tungsten Research Board,[90] published during the year, is disappointing With the exception of Prof. S J Truscott's interesting contributions relative to his experiments on the dressing of tin ores, which were referred to in last year's Reports, little information is given to enable one to judge of the progress made

A good deal has been heard of the flotation experiments being carried out at East Pool and Agar Mines, Cornwall, and according to the press[91] a demonstration of the process was recently given by M T Taylor and J. W. Partington who, it appears have discovered a reagent which secures an effective flotation of the cassiterite without bringing up the quartz and other gangue minerals

It is also said that a small commercial scale plant is being arranged for in Cornwall to test a process involving the use of anhydrous chlorine, which has been worked out in the laboratory by J J Collins   Details of the process have not yet been published

The properties of tin are referred to in a paper by E F Northrup,[92] who suggests its use in pyrometry   It melts at 232 C and does not begin to boil below 2270 C   It remains chemically uncontaminated after prolonged heating at 1680 C in Acheson graphite and wires of pure tungsten do not melt at 1680 C, and so may be used as electrodes for measuring the resistance of the molten metal   Its increase in resistivity and decrease in density with increase in temperature are of a strictly linear character and tin is therefore an excellent material for determining temperatures   The author suggests that a re-determination of the melting points of the more refractory metals should be made in terms of the resistivity of tin

The metallurgy of *mercury* has been extensively dealt with in ' The Quicksilver Resources of California '[93] by W W Bradley which should be consulted by those interested   Details of the Scott furnace are given and the operation of the rotary furnaces in use at New Idria, Cal , is also fully described   The latter type of furnace gave considerable trouble in the case of an ore containing a large quantity of free sulphur which sublimed and re-deposited instead of being burned to sulphur dioxide

The use of *calcium and other alkaline earth metals* in the manufacture of a new hard lead alloy (named   Ulco ') was described by F C

[90] *Annual Report for* 1918-19, H M. Stationery Office.
[91] *Min. Mag.*, 1919, 21, 328, 356
[92] Amer. Inst. Min. and Met. Eng ; *Engineering*, 1919, 108, 309 ; *J.*, 1919, 743A.
[93] 1918, *Bull. 78, California State Mining Bureau.*

Frary and S. N. Temple.[84]   In the course of experiments, it was found
that a considerable amount of calcium was needed to give a hardness
approaching that of antimonial lead (17 Brinell), and that this alloy
did not stand re-melting but easily lost its calcium.   Other metals of
the alkaline-earths hardened lead tő a different but marked degree.
Further experimentation showed that if two or more of the metals were
used together (apparently, a mixture of calcium and barium is pre-
ferred), the hardening effect was several times greater than when one
only was present, thus making it possible to produce an alloy, harder
than antimonial lead, but containing so little alkaline-earth metal
(well over 99% Pb) that it could be re-melted several times without
appreciable loss in hardness.   The alloy is said to be tough and pro-
duces castings free from blow-holes.   Originally designed as a substitute
for antimony in the manufacture of shrapnel bullets, it is claimed that
the alloy will take its place among the important bearing metals in view
of its high melting point, structure, and low coefficient of friction.

· *Platinum*. The difficulty of amalgamating alluvial platinum with
mercury to obtain a crude bullion at the deposit, has been met
by V. J. Zachert,[85] who amalgamates in the presence of zinc and an
electrolyte composed of a solution containing 0·05% of copper sulphate
and 0·05% of free sulphuric acid   R. E. Lyons [86] claims the production
of a platinum amalgam from platiniferous material by bringing the
material into contact with mercury and zinc in the presence of a sub-
stance capable of attacking zinc.   C. A. Logan [87] states that the use
of zinc is unnecessary and that in an acid solution of copper sulphate,
the copper plating of platinum, osmiridium, etc., and their immediate
amalgamation with mercury was possible.

The properties and uses of *glucinum* (beryllium) have been more or
less vaguely described from time to time, but, as pointed out by H.
Copaux,[88] any commercial application of the metal is impossible until
a more practical method for its isolation is available. Small samples
only of the metal have been made, so far, and nothing is known of its
properties except that it has a sp. gr. of 1·8, a melting point of 1280° C.,
and that it alloys at least to some extent with aluminium, silver, iron,
and copper. Copaux describes his method for the manufacture of
glucinum salts and their reduction to the metal by electrolysis.   J. S.
Negru [89] also gives an historical sketch of the methods hitherto employed
to isolate the compounds and metal.

    [84] *Chem. and Met. Eng.*, 1918, **19**, 523; *J.*, 1918, 737A.
    [85] *Min. and Sci. Press*, 1918, **117**, 489.
    [86] U.S. Pat. 1293828; *J.*, 1919, 328A.
    [87] *Min. and Sci. Press*, 1918, **117**, 819.
    [88] *Chim. et Ind.*, 1919, **2**, 914; *J.*, 1919, 816A, and *Comptes rend.*, 1919, **168**,
610; *J.*, 1919, 285A.
    [89] *Chem. and Met. Eng.*, 1919, **21**, 353.

ELECTRO-CHEMISTRY.

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GENERAL

THE four years of war of course led to enormous developments in the electro-chemical as in other industries, and this fact, combined with the general upheaval of markets and the transport crisis, has left producers wondering when and on what basis peace production will ultimately settle down. Countries which were exporters before the war, such as France and Switzerland, are now either suffering from over production, or are liable to do so at any moment. Other countries such as the United States, have now become exporters. And whilst it is expected that in some fields the developments made during the war may be maintained, in others it is more than doubtful. For example, the Haber process is likely seriously to trouble nitrate and cyanamide concerns.

The few typical facts and figures which follow are mostly taken from articles in the *Journal du Four Electrique.*

Sweden.—(a) In 1913, 22 electro-chemical works; in 1917, 73. (b) About 100,000 tons of electric pig iron annually, *i.e.* one-eighth of total make.

Switzerland.—(a) In 1913, 37,000 tons of carbide. In 1918, about 100,000 tons. Home consumption, perhaps 15,000 tons. (b) About 24,000 tons of ferro-silicon in 1918; home consumption, 1500-2000 tons.

France.—(a) More chlorate made in one month of 1918 than a whole year's pre-war consumption. (b) Present carbide production capacity, 100,000 tons per annum, apart from special government cyanamide works. (c) 21,000 tons of electric steel in 1913, 58,000 tons in 1918, and an actual capacity far exceeding this last figure.

Germany.—(a) Many new aluminium plants put up during the war, working up low-grade bauxite. Their future is doubtful. (b) 89,000 tons of electric steel in 1914, 220,000 tons in 1917, when it doubled the crucible steel output. (c) A great increase in cyanamide capacity during the war, as well as in Haber plant.

United States.—(a 1,200,000 tons of electrolytic copper per annum

(b) 102,000 tons of aluminium in 1918.   (c) 287 steel furnaces at beginning of 1919.   30,000 tons of steel in 1913, 305,000 tons in 1917, when the output of crucible steel actually decreased.

Great Britain.—147 steel furnaces working at the commencement of 1919.   At end of 1917, the output of electric steel was forty times its pre-war figure.

The year's published literature has contained nothing so important as to call for notice out of its place.   The above figures are, however, a testimony to the ever-growing importance of this branch of technology, and there is evidence that this growth is in many cases relative, and not merely an absolute one as the result of the war   A certain amount of " released " information has been published, and it is to be hoped that more is to come, particularly in this country.

ELECTROLYSIS—THEORY.

In those fields of electrolytic theory which have an interest for the technical electro chemist, there is little to note   Some observations on periodic phenomena in the passivity of iron made by A. Smits and C. A. Lobry de Bruyns[1] may be mentioned.   There is also an important paper by D A. MacInnes and L. Adler,[2] dealing with the mechanism of over-voltage, which makes it clearer than ever that no single theory of those so far advanced is likely to account for all the complex phenomena observed in this field.   The authors attribute hydrogen over-voltage to a supersaturated layer of dissolved hydrogen in the electrolyte surrounding the electrode, the specific effect of the latter being due to its adsorptive power for the gas   If this is high, the concentrations necessary for bubble formation are readily reached and the over-voltage will be low

INSULATORS, CONDUCTORS, ELECTRODES, DIAPHRAGMS

R. G. Allen[3] has published some data on " ermoid," an insulating material obtained as a by-product in the working up of milk   It compares somewhat favourably with red vulcanised fibre in respect of specific resistance, dielectric absorption, and the effect of moisture. The same author[4] has investigated the effect of temperature on the specific resistance of different glazed porcelains and has found the familiar logarithmic formula of Rasch and Hinrichsen to hold   Portland china and Royal Worcester chemical porcelain both gave unexpectedly high values of specific resistance.   F. B. Silsbee and R. K. Honaman[5] have carried out similar experiments for a variety of insu-

[1] *Proc. K. Akad. Wetensch.*, 1919, 21, 382 ; *J.*, 1919, 144a.

[2] *J. Amer. Chem. Soc.*, 1919, 41, 194.

[3] *Sci. Proc. Royal Dublin Soc.*, 1918, 15, 331, 405 ; *J.*, 1919, 148a, 149 a

[4] *Ibid.*, 1918, 15, 289 ; *J.*, 1919, 140 a.

[5] *J. Wash. Acad. Sci.*, 1919, 9, 252 ; *J.*, 1919, 469a.

lators, comprising different porcelains, mica and silica. They find it necessary to introduce two constants into the expression for each specimen, one characteristic of the specimen, and another expressing dependence on temperature, much the same for all substances. The specific resistance of different specimens of the same substance varied within wide limits. Their conductivity is probably largely due to traces of impurities. H. C. P. Weber and T. C. Mackay [4] have compared the effect of temperature on the dielectric constant of insulators such as waxes, paraffin, etc., and on paper impregnated with the same. The pure substances give the more favourable results. C. J. Rottmann [5] has investigated the penetration of moisture into insulating materials. No standard material examined was moisture-proof, though impregnated materials were of course better. If penetration is slow, liquid water and saturated vapour give identical results.

Little of importance has appeared on new conductors or on electrodes and diaphragms for general electrolytic work. The Westinghouse Electrical and Manufacturing Co. and S. Trood [6] prepare moulded conductors from amalgamated finely divided copper mixed with graphite, the excess of mercury being removed by heat and pressure. P. Schmidt and A. Schwieger [9] prepare hollow cylindrical or ring electrodes by spirally winding metallic wire or tape, joining up the coils by metal spraying. W. K. Page and the Clide Exploration Co. [10] patent a method for casting silicon-iron so as to obtain a product as electrode with a fine, dense, and resistant structure. Ferroso-ferric oxide, free from iron, and therefore suitable for the production of magnetite electrodes for use in acid electrolytes can be made by feeding a mixture of very finely divided pure iron oxide and hammerscale or burnt pyrites into an oxygen blast.[11] W. K. Page [12] claims to produce insoluble anodes of good conductivity by covering a core of soft iron, ferrosilicon, etc., with a coating largely consisting of magnetite and of the same coefficient of expansion as the core. Such a coating may contain $5-7\% SiO_2$ and $2-3\% Al_2O_3$, pumice, etc., the latter addition making it tougher. The mixture is fused in the electric furnace, and applied by dipping the core in the melt. The " Filtros " diaphragms patented by C. J. Thatcher [13] are of interest. Their main structure consists of coarsely grained plates or cylinders of " filtros," a siliceous material, the grains being only bonded at their points of contact. For use in alkaline electrolytes, they are soaked successively in solutions of mag-

[4] J. Franklin Inst., 1918, 186, 374; J., 1919, 180A.
[5] Ibid., 1919, 188, 409; J., 1919, 869A.
[6] U.S. Pat. 1281716; J., 1919, 20A.
[9] Ger. Pat. 313238; J., 1919, 870A.
[10] U.S. Pat. 1283280; J., 1919, 89A.
[11] Hüttenwerk Niederschöneweide, Ger. Pat. 301762; J., 1919, 912A.
[12] U.S. Pat. 1302959; J., 1919, 543A.
[13] Eng. Pat. 134116; J., 1919, 952A.

nesium sulphate and caustic soda, and finally in water. They are
kept moist by being dipped in calcium chloride or are preserved
under water until required for use.   Any silica dissolved from them
by an alkaline electrolyte is at once changed into magnesium silicate
which prevents further action, and they can be used for a long time
in hot alkali, if not too strong, without deterioration.   A normal dia-
phragm may contain 50% of voids by volume.   For use in ammoniacal
solution they are impregnated with aluminium hydroxide, for acid
solutions with hydrated silicic acid.   Alundum can be used instead of
" filtros."

PRIMARY AND SECONDARY CELLS.

The great and, as yet, unsolved problem in this field is of course
the direct transformation of the chemical energy of fuels into electrical
energy, without its previous degradation into heat energy, i e. a tech-
nically applicable method is sought of bringing about the combination
of oxygen with combustible fuel constituents by means of an electro-
lytic mechanism in a primary cell.   In this connection, an interesting
patent has been taken out by the Swiss chemists E. Baur and W. D.
Treadwell,[14] which certainly marks an advance, though it remains
to be seen to what extent their ideas are capable of practical realisation.
The sluggish rate of ionisation of oxygen, as well as of carbon and the
different fuel gases, has so far rendered cells working at low tempera-
tures impracticable   In the present case, the cells, designed to use
either solid or gaseous fuels, are kept in a heating chamber at 900° C.
The electrodes, depolarised one wi h air and one with combustible
material, are in contact over their whole surface with a diaphragm of
refractory material such as magnesia, saturated with a molten salt, such
as soda.   The electrodes themselves are not wetted by the electrolyte.
If the fuel used is solid, e g coke, it is contained in an iron vessel
and is in contact with a diaphragm consisting of burnt magnesia and
coke, impregnated with molten soda.   Above the diaphragm is a layer
of iron gauze, supporting a layer of hammer-slag, the latter surmounted
by a fire-proof dome, with air inlet and outlet.   For gaseous fuels
(hydrogen, carbon monoxide, coal-gas, water-gas) the cell consists of
an iron receiver containing melted soda, into which dip two magnesia
tubes, closed at the bottom, and lined inside with wire gauze.   Air is
led into one of these tubes, the gaseous fuel into the other   It remains
to be seen to what extent such cells are capable of large-scale economic
realisation, but there is no doubt that they mark an advance on previous
attempts, e g. on the arrangement proposed by K. A. Hofmann (see
also F. Auerbach [15]), in which molten caustic soda is the electrolyte,
becoming converted into carbonate ac a result of the working of the
cell.

[14] Eng. Pat. 126766 ; J., 1919, 469A.
[15] Z. Elektrochem., 1919, 25, 82 ; J., 1919, 375A.

Turning to ordinary primary cells, there are several developments of interest, particularly in America. A number of patents have been taken out for cells using an alkaline electrolyte. Cathodes consist of lead oxide,[16] mixtures of cupric oxide and sulphur or selenium,[17] of lead peroxide and sulphur,[18] or of an oxide and a sulphide.[19] For the more usual types of electrolyte, a mixture of MoO_3 and a basic oxide (e.g. ammonium phospho-molybdate) is recommended [20] as depolariser, and there are several methods [21] patented for the production of pure finely-divided manganese dioxide. W. O. Snelling [22] adds up to 1% metallic nickel to a granular mixture of carbon and MnO_2. L. Rabinovich and A. Mond [23] impregnate a mixture of graphite and a depolariser (pyrolusite) with a colloidal solution of the oxides of a metal (manganese) capable of more than one degree of oxidation. This is reminiscent of the use of cobalt salts [24] for prolonging the life of carbon anodes by allowing oxygen evolution to take place at a low anode potential.

The Burgess Battery Company [25] employs an electrolyte gelatinised by the addition of cereals such as maize meal, cotton starch, etc., leading to a considerably decreased cell resistance. G. N. Antonoff [26] claims the addition of weak organic acids—benzoic, tartaric, salicylic, succinic—to the electrolyte. This prevents the cell clogging up, owing to the formation of freely soluble zinc and ammonium salts. The same patentee [27] finds that the resistance of a primary cell depends on the pressure to which the depolarising mixture has been subjected, first decreasing and then increasing as the pressure rises. The optimum pressure should be found for every batch. It was of the order of 20–70 lb. per sq. inch for the mixtures used.

Little of interest to the electro-chemist has appeared on either the lead or the nickel accumulator. Patents have dealt chiefly with structural details, methods of formation of plates, etc., and present no striking features.

METAL DEPOSITION, ELECTROPLATING, AND GALVANOPLASTIC METHODS.

W. Blum,[28] in a paper read at the autumn meeting of the American Electro-chemical Society, considers the conditions which control the

[16] W. C. Bauer, U.S. Pat. 1289669; J., 1919, 407a.

[17] R. C. Benner and H. F. French, U.S. Pats. 1283653–6, J., 1919, 149a. R. W. Erwin, U.S. Pat. 1282057; J., 1919, 464.

[18] R. C. Benner and H. F. French, U.S. Pat. 1303454; J., 1919, 543a.

[19] R. C. Benner and H. F. French, U.S. Pats. 1316760–1; J., 1919, 829a.

[20] M. E. Holmes, U.S. Pat. 1281372; J., 1919, 46a.

[21] C. Ellis, U.S. Pat. 1289707; J., 1919, 149a. A. A. Wells, U.S. Pat. 1293272; J., 1919, 376a. M. L. Kaplan, U.S. Pats. 1293461–3; J., 1919, 376a.

[22] U.S. Pat. 1288722; J., 1919, 285a.

[23] Eng. Pat. 132480; J., 1919, 869a. [24] K. Jorst, Dissertation (Dresden), 1910.

[25] Eng. Pat. 128332; J., 1919, 686a. [26] U.S. Pat. 1303844; J., 1919, 543a.

[27] U.S. Pat. 1303843; J., 1919, 543a. [28] J., 1919, 866a.

nature of metallic electro-deposits, and concludes that Bancroft's
"axioms of electroplating," enunciated some years back, are essentially
sound. Concentration and nature of electrolyte, current density, and
temperature, are the most important factors. Fine-grained, bright
and hard deposits are favoured by high current density, within limits,
and low temperature.

D. McIntosh [29] discusses the optimum conditions (exact figures given)
for zinc deposition from sulphate solutions. Apart from the factors
mentioned above, colloids, and metals such as As, Sb, Cu, Co, Ni,
should be absent, and the iron content of the electrolyte should be low.
Attention has been devoted to electrolytic iron. E. H. Archibald
and L. A. Piguet [30] have investigated its deposition from ferric chloride
and ferrous sulphate dissolved in acetone, acetone-water and alcohol-
water solutions. Complete deposition is possible, but the product usually
contains carbon G. Vié [31] finds that ferrous chloride gives better
results than the sulphate. Using a strong solution of this salt, with
added sodium chloride, working at 50°-70° C. with a current density
1·6 amps. per sq. dm., and employing ordinary sheet-iron anodes, he
was able to produce continuously 99·9% iron, containing as sole im-
purity dissolved hydrogen. Until this is expelled by heat, the resulting
metal is very brittle, and can be powdered in a mortar. According,
however, to M. Schlötter,[32] an electrolyte with 150 grms. per litre of
ferrous sulphate plus 100 grms. per litre of sodium sulphate, just
neutralised with sodium carbonate, furnishes a very pure product,
almost free from hydrogen, when electrolysed at or near its boiling-
point with 20 amps. per sq. dm. There is also the advantage of being
able to use lead-lined vessels and lead coils for heating.

In the galvanoplastic and electroplating fields there has been a
certain amount of published work, chiefly devoted to improved methods
of plating on base or electro-positive metals. According to W. Thum
and J. J Mulligan,[33] base metals can be satisfactorily treated if first
covered with a gelatin film and subjected at the start to an abnormally
high current density for a short time. O. P. Watts [34] has developed an
observation of J Satka and has found that iron can be directly plated
from a copper sulphate solution, if first dipped into a bath containing
a salt of a metal intermediate between iron and copper in the electro-
chemical series, e.g. arsenic, lead, or antimony. Similarly bismuth
can be deposited on iron after a preliminary arsenic or antimony dip
and nickel on aluminium after dipping in ferric chloride. The forma

[29] *Trans Roy. Sec. Canada*, 1917 18 (iii), **11**, 113 , *J.*, 1919, 42A.
[30] *Ibid.*, p. 107 ; *J.*, 1919, 1ª A
[31] *Ann. Chim. Analyt.*, 1919, **1**, 175; *J.*, 1919, 580A.
[32] Ger. Pat. 309271 , *J.*, 1919, 908A.
[33] U.S. Pat. 1283973 ; *J.*, 1919, 79A.
[34] Amer. Electrochem Soc.; *J.*, 1919, 290A.

tion of a film of metal of intermediate potential would here appear to be the cause. Tempered or strain-hardened steel articles can be plated without deterioration if first coated by dipping with a layer of metal impervious to hydrogen, and of a melting point below the temperature at which the steel was hardened.[35] Tin is an example of such a metal which can be used with steel springs. In view of the example given, it is remarkable that, according to T. S. Fuller,[36] a coating of tin on iron increases the rate at which hydrogen diffuses through the latter.

Nickel can be plated directly on aluminium (after giving the usual preliminary cleaning treatment) if this is momentarily made the anode when first immersed in the bath.[37] The current is then reversed by a double-throw switch and deposition of nickel proceeds normally. The usual electrolyte—mixed sulphates with addition of boric acid—can be employed.

Various complex electrolytes, more particularly for lead plating on iron or steel, have received attention. A. G. Reeve[38] describes the lead-plating of the interior of gas shells, employing a slightly modified Betts fluosilicate electrolyte and working at 35–40° C. The deposition of lead, antimony, or an alloy of these metals from a solution containing tartaric, acetic, and salicylic acid salts is the subject of a patent.[39] A lead anode is employed when plating with lead, a carbon or platinum anode when depositing antimony or an alloy. Full details are given[40] for commercial lead plating on iron and steel from fluoborate solutions, including the best electrolytes for thin and thick deposits, working current densities, and temperatures. Sand blasting is preferable to pickling for the preliminary treatment.

J. Haas[41] uses a lead cyanide solution with the addition of an alkaline tartrate, D. F. Harbaugh[42] a solution of lead oxide and sugar in caustic soda. For plating copper or other metals on iron and steel, Q. Marino[43] employs a complex solution containing phosphate, tartrate, citrate, and salicylate.

O. P. Watts[44] draws attention to a case of heavy pitting which occurred during lead plating when the bath was allowed to cool overnight when out of action. On reheating the dissolved air was liberated in the form of bubbles on the cathode, with the result stated.

J. E. Woodbury[45] patents two methods by which a restricted area

[35] General Electric Co., Eng. Pat. 127177; J., 1919, 463A.
[36] Amer. Electrochem. Soc., J., 1919, 564A. [37] Metal Ind., 1919, 17, 25.
[38] Chem. and Met. Eng., 1919, 20, 388.
[39] Q. Marino, Eng. Pat. 130302; J., 1919, 727A.
[40] W. Blum, F. J. Liscomb, and others, Amer. Electrochem. Soc.; J., 1919, 907A.
[41] Metal Ind., 1919, 17, 12. [42] U.S. Pat. 1308479; J., 1919, 586A.
[43] Eng. Pat. 130446; J., 1919, 727A.
[44] Amer. Electrochem. Soc., J., 1919, 290A.
[45] U.S. Pats. 1285875 and 1291337; J., 1919, 147A, 291A.

alone of the cathode is plated, whilst at the same time excellent circulation of the electrolyte is ensured. They involve the current being carried by a small stream of electrolyte which passes (by gravity or by a pump) from anode to cathode, the electrodes being arranged one above the other A. Ness [46] places the articles to be plated in a horizontal drum, partly immersed in the electrolyte. A series of longitudinal bars is so arranged inside the drum that, by varying the direction of rotation of the latter, the articles are either immersed in the electrolyte or removed out of the drum on to an external shoot.

For the galvanoplastic production of copper sheets, the cathode can be a partly immersed horizontal cylinder, coated with a thin film of grease and rotating with a peripheral speed of 130 ft. per minute. Supplementary adjacent cathodes prevent irregular deposition at the edges. A helix of flexible non-conducting material is wound on the mandrel. After deposition, the cylindrical sheet produced is torn along the line of the helix.[17] According to the same series of patents, aeroplane propellers, manifolds for aeroplane engines, etc, are produced by starting with a layer of metal on a non-conducting core, covering this with a layer of grease or metallic amalgam, and building up to the desired thickness by successive layers of metal, separated by grease or amalgam A somewhat similar process is used for producing composite but coherent sheets of electrolytic iron. An electro-deposited layer of iron is covered by painting or burnishing with a coating of oxide not affected by the subsequent annealing process. A coating of graphite is applied to this, and the process is repeated until the desired thickness is reached.[18]

ELECTROLYTIC REFINING OF METALS.

Comparatively little has been published on this subject. H. M. Goodwin and W. G. Horsch [49] publish results on the electrical conductivity and other properties of saturated copper sulphate solutions containing sulphuric acid. Messrs. Altmayer [50] report on the U.S.A. electrolytic copper and lead refineries In the former, the multiple system is said to be gaining ground at the expense of the series system. An account by G. G. Griswold [51] of the refining of gold and silver as carried out at Perth Amboy, N.J., by the American Smelting and Refining Co., shows certain modifications in present practice when

[46] Eng. Pat. 133162 ; *J.*, 1919, 868A.

[17] M. M. Merritt and Copper Products Co., U.S. Pats. 1282261–1282270 ; *J.*, 1919, 201A.

[18] J. H. Procter and Westinghouse Electric and Manufacturing Co., U.S. Pat. 300296 ; *J.*, 1919, 866A.

[49] *Chem. and Met. Eng.*, 1919, **21**, 181 ; *J.*, 1919, 761A.

[50] *J. Four Elect.*, 1919, **28**, 121.

[51] *Chem. and Met. Eng.*, 1919, **20**, 382 ; *J.*, 1919, 181A.

compared with older published data, but no very essential changes. Of interest, as illustrating the difficulties which enemy technologists had to face during the war, owing to our blockade, is certain information dealing with the recovery of copper from anodes of bell-metal and of bronze. The former contained large proportions of nickel, lead, and zinc, and acid and copper had continually to be added to the electrolyte in quantity.[52] In the latter case an electrolyte containing alkali bisulphate is patented which is stated to prevent the transference of stannic acid to the solution, and to render possible the use of anodes with 20% or more of tin.[53] According to V. Engelhardt,[54] two large electrolytic iron plants have been producing up to 100 tons per month of refined metal in Germany during the war. It was used instead of copper.

Electrolytic Winning of Metals.

Judging from published accounts there has not been much progress in this direction. H. E. Broughton[55] writes on a process by which zinc is obtained from the fumes resulting from burning a zinc-copper pyrites. These fumes collect in the vitriol chambers and are drawn off as a sludge containing 51.6% $ZnSO_4$, 13.7% H_2SO_4, 11.6% $PbSO_4$, 16% H_2O, together with Cu, Fe, Cd, etc. After extracting and neutralising, the iron is precipitated by calcium carbonate, the solution acidified, and copper and bismuth (but not cadmium) removed by scrap zinc. The solution finally resulting (7% Zn and 3% H_2SO_4) is electrolysed in lead-lined wooden tanks with a current density of 17-20 amps per sq. ft., using lead anodes and aluminium cathodes, and gives a product 99.9% pure (0.05% Cd, 0.03% Pb, 0.02% Fe & Cu) at an energy expenditure of 2.5-2.8 kw.h. per lb. Current efficiency is low. Details are given of the arrangement of the baths and circulation of the electrolyte. Lemarchand[56] reports on a wet (sulphate) extraction process used by the Anaconda Company with a plant of a capacity of 35,000 tons per annum. A far higher recovery of silver is claimed than is got by distillation processes. The same plant is referred to in the Altmayer report.[57] Various methods are patented[58] for the purification of zinc liquors preparatory to, and for the removal of impurities accumulated during, electrolysis.

G. A. Guess[59] describes a method by which nickel is obtained from a crude matte (Ni 56, Cu 24, S 18%). This is roasted, leached with

[52] E. Pfann, *Oester. Chem. Zeit.*, 1919, **22**, 10; *J.*, 1919, 467A.
[53] Huttenwerk Niederschoneweide, *Ger. Pat.* 312941; *J.*, 1919, 911A.
[54] *Electrotechn. Zeits.*, 1919, **40**, 209.
[55] *Chem. and Met. Eng.*, 1919, **20**, J., 1919, 259A.
[56] *J. Four Elect.*, 1919, **28**, 79; *Loc. cit.*
[58] *E.g.* Eng. Pat. 126296; *J.*, 1919, 727A; U.S. Pat. 1283077; *J.*, 1919, 79A.
[59] Amer. Electrochem. Soc.; *J.*, 1919, 182A.

dilute sulphuric acid to remove most of the copper, dried, fused with charcoal, and cast into anodes (Ni 80, Cu 18, Fe 2%). The bath contains 6% Ni as sulphate, with addition of glue. Finely divided calcite is added periodically to precipitate the copper, obtained as a mud of composition $2CuO,2NiO,SO_3$, which is subsequently worked up. The working temperature is 40°–50° C., the cathode current density 13 amps. per sq. ft., and the voltage 2. The cathodes of aluminium or lead are contained in light canvas bags mounted on wooden frames. A cathodic current efficiency of 98% results, the product usually containing less than 0·001% Cu.

S. B. Christy[60] describes experiments on the recovery of gold and silver values from cyanide solutions by first depositing them on pervious cathodes of iron-wire cloth, broken carbon, etc., and then making these electrodes the anodes in a clean-up box and depositing the precious metals on sheet cathodes covered with a thin vaseline graphite layer. The anodes in the first precipitation are of iron-wire cloth, carbon, or lead peroxide. The electrodes described allow of rapid circulation and of quick and efficient work. Full details are given.

Messrs. Altmayer[61] mention in their report the electrolytic copper extraction plant of the New Cornelia Copper Co., Arizona, which has a capacity of 15,000–20,000 tons per year, and treats poor oxide and carbonate minerals by sulphuric acid leaching.

Various solutions patented for the electrolytic cleaning of metals present no particular interest. Mention should be made of an article by L. Révillon[62] on electrolytic methods for the superficial colouring of iron and copper. According to the author, the results are eminently satisfactory and durable, and are replacing painting and varnishing for certain purposes.

ALKALI AND CHLORINE.

Some papers of importance have appeared. E. Briner and others have extended and confirmed the well-known work of Foerster and of Guye on the theory of diaphragm cells by means of comparative experiments on the chlorides of sodium, potassium, and lithium[63]. A good survey of the whole subject, containing, however, nothing particularly new, is given by K. Horine.[64]

G. Yamazaki[65] communicates results obtained with a small-scale modified Castner cell, in which the mercury circulation is effected by two worm screws working in small wells. With a mercury current density of 21–25 amps. per sq. dm., and a temperature of 45°–50° C.,

[60] *U.S. Bureau of Mines, Bull.* 150; *Chem. Abs.*, 1919, **13**, 2812.
[61] *Loc. cit.*   [62] *Rev. Mét.*, 1919, **16**, 257; *J.*, 1919, 907A.
[63] *Helv. Chim. Acta*, 1919, **2**, 666; *J.*, 1920, 106A.
[64] *Chem. and Met. Eng.*, 1919, **21**, 69; *J.*, 1919, 627A.
[65] *J. Chem. Ind. Tokyo*, 1918, **21**, 1007; *J.*, 1919, 102A.

7-10N sodium hydroxide was obtained and a 99·2°ₒ chlorine (0·3 H₂, 0·2 CO₂ · O₂, 0·3°ₒ undetermined) But undoubtedly the most interesting information of the year is that contained in the "released" papers of C. F. Carrier, junr [ ] and S M Green [ ] on the Nelson diaphragm cell, to which may be added a paper by F. H. Mitchell,[ ] on the Allen-Moore cell A 1000 amp Nelson cell (the standard unit) consists of a rectangular steel tank of ¼ in plate (outer cathode compartment). This supports a U-shaped perforated cathode plate carrying the asbestos diaphragm, closed at the ends by cement mortar blocks and at the top by an inverted rectangular box of slate slabs, which in its turn supports the graphite anodes These are rectangular blocks, jointed on to lugs which pass through the slate cover and are bolted to a flat copper bar outside The brine (carefully purified) is fed into the anode compartment (simple constant-level device) and percolates through the diaphragm Steam is passed into the cathode compartment, and the caustic liquor is drawn off from the bottom The general design which as will be seen resembles the Hargreaves-Bird rather than the Townsend cell, impresses very favourably by reason of its great simplicity The average voltage over a six months' run is 3·7. Normal working liquors contain 10-12°ₒ NaOH and 14-16°ₒ NaCl The commercial guarantee (60 lb chlorine and 68 lb caustic soda from 120 lb. of salt per cell per 24 hours) is invariably exceeded The gas averages 99°ₒ pure The average energy efficiency is 60°ₒ and current efficiency 90°ₒ The anodes are treated by a method (not described) which gives them a life of 2-3 years Diaphragms last 6-8 months. Considerable flexibility (over and under-loading) is claimed and the plant can be shut down without damage Floor space and labour charges are both small Twenty plants are said to be working and 8000 cells have been installed The largest single chlorine plant in the world is the U.S. Government plant at Baltimore, where 3500 cells were erected producing 100 tons of chlorine per 24 hours This plant is fully described in Green's paper

The Allen-Moore cell rather resembles the Townsend cell in construction, the anode compartment being made of reinforced concrete, and the cathode plates, diaphragms, and cathode compartments being bolted on at the sides. The brine percolates through the diaphragm with no other opposing resistance, just as in the Hargreaves-Bird and Nelson cells. The standard unit takes 1200 ampères An average current efficiency of 95°ₒ, voltage 3·55 and energy efficiency of 62% are claimed, making 12°ₒ NaOH Anodes last 18 months, diaphragms 3 months. Overloading is possible up to 1500–1900 ampères when the voltage rises to 4·5 and the current efficiency becomes 90-92%

[ ] *Chem. and Met Eng.*, 1919, 21, 134; *J.* 1919, 411A.
[ ] *Ibid.*, 1919, 21, 17; *J.*, 1919, 573A.   [ ] *Ibid.*, 1919, 21, 370.

An installation of the well-known Billiter-Siemens cell, working at Leverkusen under war conditions, has been described.[70]

There is not much to notice in the patent literature.   H. H. Dow [71] connects together all the anode compartments and all the cathode compartments of a number of diaphragm cells arranged in series.   The liquors flow from one to the other, the brine being fed in to the first anode compartment, and the caustic liquors being drawn off from the last cell   T. Matsushima [72] has designed a mercury cell in which the cathode compartment consists of an inner tank, the bottom of which is made of a porous disc, on which rests a thin layer of mercury.   The sodium taken up at the lower surface of the mercury is converted into caustic alkali above, without the necessity of circulation.

Other Electrolytic Inorganic Products.

Of other substances, the production of permanganate has claimed most attention.   B F Lovelace and others [73] employ anodes containing manganese together with silicon, molybdenum, or tungsten.   Of greater practical interest is a study by R E. Wilson and W G. Horsch [74] on the use of ferromanganese anodes for this purpose   They used a diaphragm process, employing sheet-iron cathodes with 18% caustic soda as catholyte and 12 14% sodium carbonate as anolyte   The anodes were difficult to cast.   In addition, they became coated with a skin of oxides of iron, silicon, and manganese, which had to be removed by sand-blasting every 24 hours.   Making 8% sodium permanganate with a current efficiency of 35% and 7 volts, the energy consumption required was about 12 kw.h. per lb. of permanganate.   The most favourable current density was about 120 amps. per sq. ft.   M. de Kay Thompson [75] has also published a paper on this subject, and confirms the general results of the above authors.   Apparently the chief difficulty met with by them the insoluble skin on the anodes was connected with the exact composition of the ferromanganese, as Thompson experienced no trouble.   He used a metal containing 16·7% Fe and 6·1% C, an electrolyte containing 200 grms. of potassium carbonate per litre, iron cathodes in asbestos cloth bags. a current density of 65 amps. per sq. ft., and a temperature not exceeding 40° C.   A current efficiency of only 17% was obtained (attributed to poor diaphragms).   Using 4·2 volts, the energy consumption was about 15 kw.h. per lb. of potassium permanganate.   A conversion of up to 62·5% of the manganese was obtained.

J. G. Williams [76] has recently communicated to the Faraday Society

[70] A. J. Allmand and E. R. Williams, *J.*, 1919, 285R.
[71] U.S. Pat. 1284618 ; *J.*, 1919, 75A.   [72] Eng. Pat. 114623 ; *J.*, 1919, 361A.
[73] U.S. Pats. 1291680-2 : *J.*, 1919, 286A.
[74] *Chem. and Met. Eng.*, 1919, 20, 387 ; see *J.*, 1919, 411A.
[75] *Ibid.*, 1919, 21, 680.   [76] *J.*, 1920, 106A.

data on the technical production of sodium perchlorate, using smooth platinum anodes and iron cathodes. Commencing with a solution of 600–700 grms. of sodium chlorate per litre, a current density of 45–50 amps. per sq. dm., and a temperature of 30° C., the resistance is found to increase as the conversion proceeds. When the sodium chlorate has fallen to 50 grms. per litre, the current density has dropped to 30 amps. per sq. dm., and the temperature risen to 45–50°. Ozone is first evolved in quantity when the chlorate has fallen below 10 grms. per litre, and becomes almost unbearable at 5 grms. per litre. An average current efficiency of 85% is obtainable at the temperatures given. A higher temperature reduces the voltage more rapidly than it does the current efficiency. A certain amount of chloride is formed, rather greater the higher the temperature. At low temperatures, slight alkalinity does not appear to matter; at higher temperatures it pays to avoid this by regulated addition of acid. A cell for perchlorate production is described [77] in which a thin stream of electrolyte is made to flow alternately upwards and downwards through a series of water-cooled cathode chambers very nearly filled with U-shaped platinum plate anodes, maintained at the right distance from the cathodes by insulating shoes.

A further careful study of the electrolytic production of perphosphates has been published [78]. To produce these salts successfully, the current density must not be too high (2–3 amps. per sq. dm.), solutions must be concentrated, and there should be about 2·6 equivalents of base present to 1 molecule H_4PO_4. The current efficiency falls off as the electrolysis proceeds, but a 64% conversion can be reached. The addition of potassium fluoride does not appear to affect the anode potential, as had hitherto been supposed. The mechanism of the oxidation is supposed to be

$$P_2O_7'''' + OH' = P_2O_8'''' + H + 2e$$
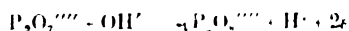
K. and E. Jellinek [79] publish a further elaborate paper on the electrolytic production of sodium hyposulphate $(Na_2S_2O_6)$, containing a vast amount of detail (particularly on the most suitable choice of electrodes) which cannot be gone into here. A 7% solution has been obtained.

In connection with the condensation of acetylene and water to acetaldehyde by means of mercuric oxide, methods for producing this substance electrolytically by making mercury the anode in caustic soda solution have been described. H. W. Matheson [80] uses a cast-iron pan, 6 ft. in diameter and 15 in. high, containing the mercury, a nickel or iron cathode, and 3–10% caustic soda solution. A current

[77] C. I. (1914) Synd., and others, Eng. Pat. 125608; J., 1919, 462A.
[78] F. Fichter and A. Rius, Helv. Chim. Acta, 1919, 2, 1; J., 1919, 220A.
[79] Z. physik. Chem., 1919, 93, 325; J., 1919, 411A.
[80] Eng. Pat. 132560; J., 1919, 819A. Canad. Chem. J., 1919, 3, 259; J., 1919, 793A.

density of 55 amps. per sq. ft. and 8 10 volts are employed. Strong agitation is necessary to keep the oxide formed from settling on the mercury. A similar, though less simple, apparatus is employed by H. Danneel and Elektrizitätswerk Lonza A.-G.[81]

ELECTROLYTIC ORGANIC PRODUCTS.

C. J. Thatcher[82] gives a general review of the possibilities in this field. He has prepared several tons of p-aminophenol sulphate by an electrolytic method

J. Feyer[83] has examined carefully the formation of chloroform from acetone and from alcohol. He used neutral solutions of alkali or alkaline-earth chlorides, no diaphragm, a platinum anode, and tried cathodes of various metals (platinum, nickel, copper). An auxiliary cathode, in a diaphragm, taking up to one-third of the current, was employed to keep the electrolyte neutral. Using acetone, added little by little to avoid reduction at the cathode, a current efficiency of 60 70% and a conversion of 80% were obtained 6 7 volts were necessary at an anodic current density of 2 5 amps per sq cm. The concentration of the electrolyte within limits did not matter, but the absence of iron was important With alcohol, the results were better Thus, with a similar current density, a 90% current efficiency and a 99% conversion were obtained, using calcium chloride. The product was very pure.

Work on the electro chemical oxidation of phenol and the cresols has been continued[84] A variety of dihydroxy derivatives and their condensation products can be obtained by varying the conditions, and, by pushing the oxidation further, the benzene ring can be broken down, giving such compounds as fumaric and succinic acids, as well as carbon dioxide and monoxide.

K. P. McElroy[85] patents the production of glycols from olefines, oil-gas, etc The electrolyte is a brine solution. A diaphragm is immaterial. The gases are blown in at 4 5 atmospheres pressure, and should always be present in good excess. The anodes are of lead, platinum, or carbon. The presence of catalysts, such as platinum or palladium black, cerium, manganese, or chromium salts, helps the reaction.

FUSED SALT ELECTROLYSIS.

There is little to record under this head. It is known that great progress has been made during the war in the production of magnesium, e.g. at Shawinigan, but very little has been published. G. O Seward

[81] Ger. Pat. 311173 ; J., 1919, 576A.
[82] Chem. and Met. Eng., 1919, 21, 663.
[83] Z. Elektrochem , 1919, 25, 115 ; J., 1919, 599A.
[84] F. Fichter and F. Ackermann, Helv. Chim. Acta, 1919, 2, 583 ; J., 1919, 857A.
[85] U.S. Pat. 1308797 ; J., 1919, 658A.

has two interesting patents   In one[86] he uses a triple fluoride electrolyte (magnesium, barium, sodium) of specific gravity 3·2 and m pt. 835° C.   Magnesium oxide or carbonate is added continuously to this, and the electrolysis carried out in a carbon lined pot resembling an aluminium furnace, using carbon or graphite anodes, and starting with a layer of copper as cathode at the bottom of the cell   The magnesia remains suspended in the electrolyte and practically no fluorine is liberated.   By the use of more complex mixtures an electrolyte melting at 680 can be obtained but 950 is a favourable electrolysis temperature   In his second patent[87] he employs an electrolyte of specific gravity 4·1 (MgF₂ 55, NaF 5, BaF 40%) covered with a thick layer of magnesium oxide or carbonate   A cast iron container with a cooled base is used as electrolyser anodes of carbon and cast iron cathodes projecting upwards and pointed to assist in the detachment of the magnesium   The latter rises to the top of the cell

A similar change from the ordinary procedure, but in the opposite direction, is suggested by A M Weaver[88] who proposes to prepare aluminium from an aluminium chloride sodium chloride bath   A M Goldschmidt[89] describes the extraction of alumina from labradorite This is crushed, treated with 30% nitric acid and the mixture of dried nitrates heated to a definite temperature sufficiently high to decompose the aluminium but not the sodium or calcium salts   The latter are then leached out   The alumina is freer from iron than that obtained from clay   The manufacture of aluminium as carried out at Horrem in the Rhine Province has been described[90]

T. R. Forland[91] gets molybdenum by electrolysing a fused mixture of the chlorides of sodium, aluminium and molybdenum melting below 200° C.

ELECTRIC FURNACES AND ACCESSORIES

A good general paper on electric furnaces dealing chiefly with their use for metallurgical work was read by H Etchells[92] before the Faraday Society   Towards its conclusion he discusses in an interesting way such questions as power factor graphite versus carbon electrodes for steel furnaces electrode holders of minimum contact resistance, protection of electrodes against burning etc   The subsequent discussion also contains points of interest   Three other publications should be mentioned   R C Gosrow[93] contributes a valuable paper on electric furnace design which although specially referring

[86] U.S. Pat. 1310449; J., 1919, 643A

[87] U.S. Pat. 1310450; J., 1919, 643A

[88] U.S. Pat. 1297946; see J., 1919, 375A

[89] Tidskrift Kemi 1919, 16, 21; Chem. U., 1919, 13, 1975

[90] J., 1919, 303B.   [91] U.S. Pat. 1305350; J., 1919, 586A.

[92] Trans. Faraday Soc., 1919, 14, 71; J., 1919, 375A

[93] Chem. and Met. Eng., 1919, 21, 235; J., 1919, 780;

throughout to ferromanganese practice, is full of practical points applicable to all types of furnace. H. M. St. John [94] deals with the commercial testing of metallurgical electric furnaces, and discusses the many aspects from which these tests must be approached. F. E. Hill and A. P. M. Fleming [95] read (before the Faraday Society meeting mentioned above) a paper on the control of electric furnaces, describing and comparing the various possible ways of effecting this. The account given is a clear one, and the diagrams are good.

Furnaces of new pattern will in general be considered when dealing with the particular processes for which they are designed. One exception, however, must be mentioned here—the electrodeless high-frequency induction furnaces developed by E. F. Northrup,[96] and patented by the Ajax Metal Co.[97] In these furnaces electro-magnetic energy of very high frequency (10,000–25,000 cycles) is converted into heat without any interlinkage with iron. An intermittent oscillatory discharge from condensers can be employed up to about 100 kw., but for large units, an electric generator coupled up directly with a steam turbine will probably give the best results. An oscillatory current system involves expensive condensers and gives a low power factor, whilst using an alternator, the power factor is practically unity, and units of 1000 kw. can be designed. The possible voltage is only limited by considerations of safety. Rapid heating, high and uniform temperatures, high thermal efficiency, and good control are all claimed. Further, non-conducting material, such as glass, can be treated as easily as metals. Metals can be melted *in vacuo* and in absence of carbon. With a small laboratory unit, batches of several kilos. of glass, electrolytic iron, nickel, and platinum have been melted in a few minutes. The method appears to have very considerable possibilities for many kinds of fine work.

Apart from this, the most interesting development in electric furnace design is the attention which is being paid to reducing the consumption of electrodes by protecting them from air at the points where they enter the furnace, a number of incidental advantages being secured at the same time. Thus J. R. Hoyle and P. W. Fawcett [98] have a conical chamber, composed of two hinged segments, the base of each resting on the water-cooled ring through which the electrode enters the furnace, the upper and narrower ends fitting against the electrode, which slides through them. C. C. Gow [99] provides for a closely-fitting sleeve, engaging at the bottom with an annular seating which can slide over the

[94] *Chem. and Met. Eng.*, 1919, **21**, 377 ; *J.*, 1919, 866A.
[95] *Trans. Faraday Soc.*, 1919, **14**, 90 ; *J.*, 1919, 375A.
[96] *Chem. and Met. Eng.*, 1919, **20**, 381 ; **21**, 258 ; *J.*, 1919, 292A, 777A.
[97] Eng. Pats. 111844 and 119220 ; *J.*, 1919, 225A, 375A.
[98] Eng. Pat. 130205 ; *J.*, 1919, 686A.
[99] Eng. Pat. 130687 ; *J.*, 1919, 829A.

furnace casing in any direction, The upper part consists of several superposed layers of magnetic material of progressively changing diameter, so arranged that by the attraction of the current, they form a self-adjusting sealing gland irrespective of the diameter of the electrode at the particular point A Stobie [100] describes a simple form of protection consisting of a light metal cylinder, 2 ft long, and a few inches wider than the electrode fixed on the roof of the furnace around the latter A sealing plate is put on top of this, and prevents the passage of the flame whilst this in turn is sealed by throwing on to it a little gamster For furnaces with short electrode travel, a device is used consisting of a number of short concentric cylinders fitting inside one another, so as to form a telescopic tube According to this author, 75% of the usual electrode consumption in steel furnaces (up to 20 lb. per ton or more) can thus be saved J C King [101] and W R Mott [102] coat the electrodes themselves with a layer that will resist oxidation, using respectively a baked-on mixture of carbonaceous binder with magnesite or dolomite, and a coating of copper or other metal not attacked by carbon at a high temperature, with an outer layer of nickel

Electrode consumption is also being generally lowered by the more frequent introduction of continuous feeding of electrodes, fresh electrodes being jointed on above as required, either by male and female, or by nipple joints The loss of stump ends is thus avoided, though a good deal of trouble is sometimes caused by the threads (machined for graphite, moulded for amorphous carbon) crushing, and the stumps falling off

Several papers have appeared on the manufacture of electrodes, e.g. by T R Hay [103] and by G H Spencer [104] The former is particularly full of information the latter deals with the manufacture at Shawinigan Another paper describes a gas-fired annealing furnace used in the manufacture of amorphous electrodes [105]

There should be mentioned an investigation by R A Hadfield and S A Main [106] on the radiographic examination of carbon electrodes with a view to detecting flaws and predicting breakages From this last point of view the results are so far negative.

There is a distinct current of opinion setting in in favour of the use of graphite as against carbon electrodes, particularly for large furnaces, and now that electrode losses are being cut down Their much higher current carrying capacity gives them a great advantage

[100] *Engineering*, 1919, **107**, 749
[101] U S Pats. 1312255 1312261 ; &. 1919. 687A
[102] U S Pat. 1314693 . *J* . 1919. 830A
[103] *Raw Material*, 1919, **1**, 262   [104] *Canadian Chem. J* , 1919, **3**, 270.
[105] *Elect. Times*, 1919, **55**, 131   [106] Faraday Soc . Apr 29 ; *J.,*1919, 424A.

ELECTROTHERMAL METALLURGY—GENERAL.

This is perhaps the field in which there is most to report. Electric steel furnaces have come into their own during the war, particularly in this country, which, in previous years, had lagged far behind its rivals in this respect. There is also no doubt but that electric pig-iron furnaces have a big future before them, and that perhaps in unexpected quarters. Electrical methods applied to non-ferrous metallurgy have made great strides. At présent this progress is chiefly apparent in melting operations, but good work has been done on the winning of metals, particularly of zinc, where the former great difficulties are being surmounted with success.

A number of patents should first be noted on new furnaces for the melting and refining of metals in general. E. Grammont [107] in his arc furnace has a conducting hearth consisting of a metal plate covered with an intermediate layer of conducting agglomerate (carbon, pitch, tar) and an upper layer of non-conducting refractory. A number of wells are provided at intervals in this upper layer. It is claimed that the convection currents thus produced bring about good mixing of the molten charge. J. Thomson [108] patents two types of resistance furnaces. In one a carbon resister is suspended above a melting tank along its longitudinal axis. The heat produced is reflected down by the covering arch. In the other, crucibles containing the metal rest on a zig zag carbon resister, the heat being communicated to them by conduction. A combined arc-induction furnace has been designed, [109] provided with a number of channels in the hearth, separated by insulating material. By suitably arranging the transformer windings, heat is developed in these channels, and leads to brisk circulation and good mixing. There is nothing novel about the arrangement of the arc or arcs. The Ajax-Wyatt [110] furnace is also an induction furnace, provided with a loop channel, below and communicating with the bath of molten metal. One leg of the transformer is threaded through this channel, being nearer to the metal at a point where the channel is constricted than elsewhere. Unidirectional circulation with strong mixing results. So far only monophase furnaces of up to 100 kw. have been designed. With two- or three-phase current, a power of 300 kw. could be absorbed. J. D. Shipton [111] suggests an indirect arc furnace, the heat being radiated on to the metal, with an arrangement for preheating the charge in the upper part of the chamber. I. Rennerfelt [112] provides for several vertically suspended electrodes from

[107] Eng. Pat. 120786; *J.*, 1919, 80A.
[108] U.S. Pats. 1308877 and 1308880; *J.*, 1919, 643A.
[109] Ger. Pat. 309087; *J.*, 1919, 645A.
[110] *Chem. Abs.*, 1919, 13, 399; U S. Pat 1312069; *J*, 1919, 687A.
[111] U.S. Pat. 1313746; *J.*, 1919, 827A.
[112] U.S. Pat. 1313834; *J.*, 1919, 830A.

which arcs pass to a central carbon projection in the bottom of the furnace. A number of crucibles are arranged on the hearth in the heating zone of the arcs. The Société Electrometallurgique Française[113] patents a carbonaceous conducting crucible hearth to which current is led at several points by conductors fitting into and projecting beyond the same. These are connected outside to a neutral point, and the hearth is heated by three-phase current. A good general paper by H. A. Greaves[114] may finally be noted, in which he compares the different types of furnaces used for melting metals.

ELECTRIC STEEL

Steel refining still remains the biggest field for the electro-metallurgist. Attention should first be drawn to the Faraday Society papers already mentioned, particularly to those by H. Etchells[114] and J. Bibby,[116] and to the ensuing discussion. The former author compared the three types of furnace chiefly used in this country, viz. the Héroult, Electrometals, and Greaves-Etchells, and set out in particular the claims of the last. He laid particular stress on the automatic regulation of short circuit disturbances due to the particular design employed (two sets of electrodes and the hearth connected in star, the latter also being earthed). He also claimed as a new feature the freedom from chilling caused by the lining, owing to the current passing through the same. Bibby devoted the main part of his paper to the Electrometals furnaces describing 2, 3 and 4 phase types, the last of 20 tons capacity. Mention was made of flexible packing glands round the electrodes preventing oxidation. H. A. de Fries and J. Hertenius[117] describe recent improvements in the Ronnefelt furnace. A larger hearth area for the same charge gives a bigger area of contact between the slag and the metal, and this, added to the greater power of the furnace, leads to more rapid work. The side electrodes can now be tilted so that arcing can take place between them and the slag, and then back to the central electrode. This procedure is used when the charge is molten—free-burning arcs are employed for melting scrap. The dome-shaped roof is now removable which facilitates repairs to the lining. C. H. Vom Baur[118] describes his furnace, the shape of which is so designed as to ensure even consumption of the refractory lining on the walls. W. K. Booth[119] deals with the Booth-Hall furnace which has a hearth which becomes conducting when well heated up. An auxiliary electrode is provided which allows the furnace to function as a free-burning arc furnace until this has happened. A report pub-

113 Eng. Pat. 123306, J., 1919, 91A.   114 Electrician, 1919, 83, 256.
115 Trans. Faraday Soc., 1919, 14, 71. J., 1919, 375A.
116 Ibid., p. 79; J., 1919, 368A.   117 Iron Age, 1919, 103, 190.
118 Chem. and Met. Eng., 1919, 20, 488, see also J., 1918, 156A, 422A.
119 Engineering, 1919, 107, 656.

lished in *Blast Furnace and Steel Plant* [120] contains some interesting
points. Induction furnaces have been very little developed in the
U.S.A., as in this country (see J. Bibby, *loc. cit.*). For furnaces dealing
with molten charges, 3000 kw. (30 tons capacity) for a three-electrode
furnace, is about the maximum size advisable at present. 25-cycle
current gives a better power factor than 60 cycles. With the latter it
does not pay to go beyond 15 tons. Cold-melting furnaces exist of
capacity up to 10 tons. A discussion published in the *Electrician* [121]
brings out a number of practical points, as does a paper by R. G.
Mercer,[122] who deals particularly with the question of electrode econ-
omy and electrical details. W. E. Moore [123] discusses the production
of steel castings and J. A. Coyle [124] describes the preparation of nickel-
manganese steels in the Héroult furnace, using cold scrap, ferroman-
ganese, and nickel, with lime and fluorspar. F. E. Bash [125] has com-
pared the tapping temperatures in a large number of cases for open-
hearth and arc furnaces The results obtained were remarkably
constant, and it is interesting to note that the electric furnaces almost
invariably gave rather lower temperatures

Of new furnaces, a few only need notice A. Sahlin [126] has a somewhat
complicated arrangement with a number of pairs of electrodes entering
the furnace in the same vertical plane, but at different angles. The
lower electrode of each pair, and also the hearth electrode, when pro-
vided, are earthed. Depending on the nature of the charge, the arcs
can be free-burning or can go to the slags. G. H. Benjamin [127] patents
a furnace with a rotating hearth capable of relative movement with
respect to the body. J. H. Gray [128] tilts his furnace about a centre in
line with the top of the roof so that the electrode, provided with a
cooling ring in contact with the roof, does not move from its working
position.

" Synthetic " Cast Iron.

One development, which has taken place in several countries, but
which has only a doubtful chance of surviving war conditions, is the
production of high-grade cast iron in the electric melting furnace from
steel scrap (chiefly turnings). In France the lead was taken by C. A.
Keller,[129] who sacrificed his 1908 patents. The process consists essen-
tially of simultaneous melting and carburising. For white cast iron,

[120] 1919, **2**, 498 ; J , 1919, 905a.   [121] *Electrician*, 1919, **82**, 563.
[122] *Iron Age*, 1919, **103**, 1497.   *Chem. Abs.*, 1919, **13**, 1973.
[123] Amer. Electrochem Soc. ; J , 1919, 420a.
[124] *Chem. and Met. Eng* , 1919, **20**, 618 , J., 1919, 582a.
[125] *Bull. Amer. Inst. Min. Met. Eng.*, 1919, 1739.
[126] *Engineering*, 1919, **107**, 655 ; J., 1919, 467a.
[127] U.S. Pat. 1314384 ; J., 1919, 779a.
[128] U.S. Pat. 1313890 ; J., 1919, 830a.
[129] Iron and Steel Inst., Sept. ; J., 1919, 771a.

turnings, basic slag. and charcoal or small coal constitute the charge.
The first melting removes the phosphorus and carburises up to 1%, -
a second melting desulphurises and carburises further. A very satis-
factory product (C 2·9, Si 1·75. Mn 0·5, P 0·05%, S trace) results. The
Société Keller et Leleux at Livet have been making up to 300 tons per
day from the middle of 1916, employing four 2000 kw. furnaces and one
of 2500 kw. Another Government installation at Nanterre was making
a similar quantity, employing 10,000 kw.[130] R. Turnbull[131] discusses
the outlook in Canada, where about 1000-5000 tons per month of a
similar product (C 3·3·5 Si 1·1·4 Mn 0·7, P 0·02 S 0·015%,) was being
made at the time of the armistice, at a cost of 24 lb. of electrodes and
rather over 500 kw.h. per ton. Both in France and in Canada a supply
of scrap is the first necessity. but whereas the question of the price
of power is looked on as important in France Turnbull regards as the
second essential in Canada the return of the specifications for cast iron,
relaxed during the war. to their old normal standards (not more than
0·01% of each S and P) Bell[132] also has an article on the production
of grey cast iron. The furnace used ran through 13 heats of 625 lb
per 24-hour day, using 8 lb of electrodes and 650 kw.h per ton. The
quality of the product and the ease of making special mixtures rendered
competition with the cupola possible. These features are also insisted
on in France. where it is pointed out that the product is really a high
carbon steel. A patent has been taken out in this country by G. J.
Stock.[133] G. K. Elliott[134] proposes to supplement the cupola by a
basic electric furnace for superheating and refining high grade and high
melting grey cast irons. for which purpose the lower temperature of
the cupola is inadequate.

Electric Pig Iron

The direct electric smelting of pig iron from ores is gradually gaining
ground. A. Stansfield[135] deals with the problem very thoroughly
from the point of view of the conditions of British Columbia, discussing
available ores and power. and comparing the Electrometals furnace
with those designed by Helfenstein and by Noble. J. Babby[136]
describes furnaces of the Electrometals type. of capacities from 7000-
31,000 tons of pig per year (2500-10,000 h.p.) He predicts that a
furnace taking 6000 h.p. with 8 electrodes and an annual production
of 18,000 tons of metal will prove the most popular. Using 60% ore

[130] J. Four Elect. 1919. 28, 148
[131] Chem. and Met Eng. 1919. 20, 178.
[132] Can. Machinery, 1919. 21, 7; Chem Abs. 1919. 13, 1442
[133] Eng Pat. 130343. J. 1919. 727A.
[134] Amer. Electrochem Soc : J. 1919. 417A
[135] Chem. and Met Eng. 1919. 20, 630
[136] Engineering. 1919. 107, 649, J. 1919. 466A

and producing gases with 22% CO_2, a ton of pig can be produced at a cost of 6 cwt. of coke and 1500 kw.h. per ton.   70% of the coke used in blast furnace smelting is saved, and a balance in this respect is struck between the two processes when the price of 1 h.p. year equals that of 2·3 tons of coke.   A Frankignoul [137] has taken out two patents.   In the one, the ore is reduced in a shaft furnace by gas generated in a separate producer and preheated to 1500 C before entering the tuyères, the spongy iron being refined electrically on the hearth below. In the other patent, tuyères and electrodes are on the same level, the latter as nozzles arranged axially to the tuyères proper, and entering the furnace through the tuyère openings

G. M. Colvocoresses [138] describes a novel way of treating Sudbury ores (complex copper-nickel iron sulphides) which utilises the iron, hitherto wasted, viz by treating the ore as an iron ore, roasting it, smelting it to an alloy pig iron, and refining the latter to " Nicu " steel   The trials were carried out using electrothermal methods for both smelting and refining   Successful blast furnace operation is anticipated, and the open hearth could be used for the steel.   The " Nicu " steel contained Ni 2·13, Cu 0·4, C 0·2, Mn 0·51, S 0·03, Si 0·03, P 0·006% and satisfied Government nickel steel specifications.   Provided that the proportion of copper does not exceed $\frac{1}{8}$ to $\frac{1}{4}$ that of the nickel, the former can apparently be substituted satisfactorily for the latter, even up to 0·8% Cu.   A recovery of 98% Cu, 98% Ni, and 96% Fe on the original ore was reached, compared with 83% Cu and 80% Ni when the ore is treated as a nickel copper ore

ELECTRICAL HEAT TREATMENT

One last feature should be noted in ferrous metallurgy   the development of electrical heat treatment furnaces.   W. F Jones [139] employs an electric muffle furnace, the resistance elements being inside, the whole being evacuated, and vacuum locks being provided for the introduction and withdrawal of the articles treated.   The oxygen is removed chemically from the residual air.   A. M. Clark [140] describes the furnaces of the General Electric Company, [141] which are vertical in type and built up in successive cylindrical sections.   The low-temperature form (up to 510 C.) has the heating units of calorite ribbon mounted on insulators inside the furnace   In the high-temperature form (up to 1000 C.) heavy calorite ribbon, mounted on insulators, is embedded in the refractory brick wall   Automatic control is provided, and uniformity of speed and constancy of heating, as well as avoidance of

[137] Eng. Pats. 125194 and 130198 ; J., 1919, 372A, 728A.
[138] Trans. Canad. Min Inst. 1918, 21, 48 ; J , 1919, 326A.
[139] Eng. Pat. 120944 ; J , 1919, 77A.
[140] Blast Fur. and Steel Plant, 1919, 7, 343 ; J., 1919, 639A.
[1] E. S. Collins, U.S. Pats. 1281521 and 1310060 ; J., 1919. 46A, 644A.

scale and elimination of skilled labour are claimed. Another paper [142] contains a description of such an installation of 100 kw. units. in operation for heat treatment of gun forgings. J. A. Fleming [143] also has a heat-treatment furnace in which the current is carried by loops of nichrome. Furnaces of 200–300 kw. are mentioned, easily reaching 1000°–1200° C. The Morgan Crucible Co. [144] has developed an electrically-heated tube furnace, taking 10° volts. T. F. Baily [145] has written a review of different furnaces proposed.

FERRO ALLOYS.

A description [146] has appeared of work carried out at the University of Melbourne during the war on the production of ferro-chrome and ferro-tungsten, using a small furnace of Héroult type. Many details are given, which cannot be included here. J. W. Evans [147] gives an account of the war manufacture of ferro-molybdenum in Canada from molybdenite concentrates. Vertical, cylindrical, monophase furnaces were employed taking 3000–4500 amps. at 50 volts. Using a concentrate with 75% MoS_2 and 9% Fe, and adding a little scrap steel to the charge, 1050 lb. of 70% alloy could be obtained in 24 hours, tapping every 6 hours. 100,000 lb. of alloy was made during two years. H. Thaler [148] patents the electric furnace production of ferro-manganese from low-grade manganiferous slag. This is fused in a non-oxidising atmosphere, with iron, carbon, and lime.

ELECTROTHERMAL WINNING OF NON-FERROUS METALS.

According to Lemarchand [149] the great increase in production of zinc in allied countries during the war was due essentially to electrothermal and electrolytic methods. He gives no details of such developments, contenting himself with outlining the already familiar processes due to De Laval and to Côte and Pierron. C. H. Fulton [150] however, gives full details of quite a new method. Oxidised zinc ore or roasted concentrate is mixed with crushed coke and pitch and formed into briquettes of large size, which retain their shape during and after the distillation of the zinc from them. They conduct the current, and themselves form the resistors. The fuel employed is 60–85% of the weight of the ore, as against 40–50% in ordinary smelting but the briquettes themselves can be burnt after the zinc is been distilled off. They weigh about 90 lb. when made and lose 20–50% of their weight on heating. Practically all the zinc is distilled off, but, by careful

[142] *Iron Age*, 1919, **103**, 673.
[143] *Engineering*, 1919, **107**, 416.
[144] *J. Four Elect*, 1919, **28**, 84.
[147] *Trans. Can. Min. Inst.*, 1918, **21**, 154; *J.*, 1919, 326A.
[148] Ger. Pat. 307393; *J.*, 1919, 194.
[145] Eng. Pat. 131061; *J.*, 1919, 830A.
[146] *Elect. Rev.* (Chicago), 1919, **75**, 149.
[149] *J. Four Elect*, 1919, **28**, 78.
[150] *Bull. Amer. Inst. Min. Met. Eng.*, 1919, 2159.

control, much lead remains in the briquettes and can be subsequently
recovered by smelting. A typical furnace of small size took 36 such
briquettes, mounted in three groups of columns which were connected
in star The total charge contained 1700 lb. of ore, and three such
charges could be smelted in 24 hours A larger furnace is to deal with
$8\frac{1}{2}$ tons of concentrates in the same time The different columns are
connected above and below by graphite blocks and discs. The cover
of the retort is movable Without preheating the retort, 1 ton of
60% ore could be distilled with 2200 kw h , and with a 95 100% recov-
ery. Advantages are claimed with respect to recovery, labour, upkeep,
thermal efficiency, and general applicability to different kinds of ore

An electrothermal zinc smelting plant operating near Cologne has
also been described.[151] The furnace again is of resistance type but
the charge of ore and coke, containing a much lower proportion of the
latter than in the process described by Fulton, is not briquetted The
zinc recovery would appear to be poor F. A J Fitzgerald [152] de-
scribes a small radiant resistor furnace for the distillation of zinc
from low grade or scrap materials. Rather more than 1 kw h per
kilo of refined zinc is required, starting with fused metal Condensa-
tion difficulties have been completely overcome.

There is little to report with regard to other metals Considerable
progress would appear to have been made in the electro-smelting of
copper in the United States, but no accounts have been published   P
Papencordt [153] has done experiments on the working up of complex
speisses from Oker a H a problem which has presented difficulties
in the past from the point of view of the separation and recovery of the
rare metals The general idea was to smelt electrically in a graphite
crucible furnace with the addition of pyrites, the arsenic being volatil-
ised as sulphide, and the excess of sulphur combining with the metallic
constituents of the speiss This was found possible, a matte being pro-
duced containing 87% of the copper, 12% being retained in a speiss
rich in antimony, and the remainder going into the slags The copper
in the speiss was recovered by roasting with sodium sulphate and
lixiviating, the antimony going to Na_3SbS_3 M J Sigrist [154] reports
successful trials on the electrothermal production of sulphur-free ferro-
nickel from New Caledonian minerals. A product with Ni 55-60,
C 0.5 0.6, Si 0.1 0.2, and S 0.02 0.03% finally resulted. The nickel
losses were inappreciable. B. G. Klugh [155] reports on the production
of silico-manganese under war conditions from low-grade raw materials.
An open, rectangular, carbon-lined furnace was used, with three elec-
trodes in line and three-phase current. The reducing agent was bitu-

[151] *J.*, 1919, 303R.   [152] Amer. Electrochem. Soc.; *J.*, 1919, 823A.
[153] *Metall u Erz,* 1919, **16,** 6 : *J.*, 1919, 223A.
[154] *J. Four Elect.,* 1919, **28,** 55.
[155] Amer. Electrochem. Soc.; *J.*, 1919, 638A.

minous coal. From ores averaging 25% Mn, he produced an alloy with Mn 65, Si 21, Fe 13%, at an expenditure of 9000 kw h. per ton, and a 73% recovery of metal. Slag containing 1% Mn was also smelted with iron turnings. A metal of composition Mn 70, Si 20, Fe 9% was obtained at an expenditure of 15 000 kw h. per ton E. S Berglund [156] patents an hermetically closed electric furnace for dealing with lead ores, the molten lead being drawn off through a siphon, and the furnace condenser being water-sealed.

FUSION AND REFINING OF NON-FERROUS METALS AND ALLOYS.

Most of the literature in this section refers to brass melting. Several new furnaces have been devised in the course of the year.

H. M. St. John [157] describes a rocking arc furnace, consisting of a cylindrical steel shell, lined with refractories, that can be rocked up to a maximum arc of 200 by rollers and ring gears Horizontal axial adjustable electrodes of graphite are used. A 300 kw unit can melt up to 1500 lb. of brass per hour, including all incidental operations, at an average expenditure of 250 kw.h per ton of yellow and 275 kw.h. per ton of red brass The losses for clean metal are respectively less than 1% and 0.5%, and the electrode expenditure 2 3 lb. per ton. The usual claims of reliability uniformity of temperature, etc , are made, and it is stated that difficult mixtures. e.q those containing much lead, can be dealt with The lining lasts on an average 350 heats The greater part of it is continually washed by the molten metal and is also 18–20 in from the arc. C. H. Booth [158] describes a similar furnace, which, however, does not rock. but rotates at two revolutions per minute. Starting with a hot furnace a charge can be put through in 30 40 minutes, at a consumption of 240 300 kw h per ton. Metal losses are very low. e q. 1 lb in 250 lb with a 50 : 50 brass Rated capacities vary between 250 and 3000 lb. The usual claims are made. E. F. Collins [159] gives an account of a furnace with a resistor of granular coke on each side of the melting hearth, and discusses fuel-fired and electrical furnaces from the point of view of metal losses. The Morgan Crucible Company [160] have put on the market two types of electric carbon crucible furnace. The small size, intended particularly for brass melting, has a capacity of 200 lb. Water-cooled electrodes are provided above and below, and the crucible is so designed as to produce heat where it is most needed The spout is heated. The larger size, intended for three-phase current. takes 800 lb. of metal, and tilts

[156] Eng. Pat. 114303 : J., 1919. 78A
[157] Chem. and Met. Eng., 1919, 21, 13.
[158] Chem. and Met. Eng , 1919, 21, 636.
[159] Chem. and Met. Eng., 1919, 21, 673.
[160] Eng. Pats. 129407, 129760 ; J., 1919, 685A, 686A. Engineering, 1919, 107, 416.

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about the spout as a centre. Temperatures of 1300° C. can be reached. At present 15 kw.h. are necessary per 100 lb. of metal, but an improvement is looked for.

H. W. Gillett [161] has an excellent review, dealing with the whole question of brass furnaces, first of all comparing their performance with that of fuel-fired furnaces, and then discussing the relative merits of five proved commercial types. This paper should be consulted by anyone interested in the subject. T. F. Baily [162] describes his well-known resistor furnace, whilst another paper [163] gives details of its performance in practice, it having been employed with success, amongst other things, for melting zinc cathodes and phosphor-bronze. An anonymous paper [164] on bronze fusion might also be mentioned as containing details of interest, as also one on the preparation of cobalt chromium-tungsten alloys in an electric furnace of the arc type. [165] The induction furnace has been much used in Germany during the war to recover tin from rich bronzes, etc [166]

CARBIDE AND OTHER PRODUCTS.

There is little of interest in the patent literature on carbide. J. H. Reid [167] patents a furnace with a raised conducting support or hearth, immediately below and between the electrodes. The carbide formed on this flows away, whilst unreacted material remains. If necessary the support can be electrically heated to assist the flow the carbide and application of an electro-magnetic field will allow the position of the zone of greatest heat to be varied. The use of various types of briquetted charge is patented by F. M. Becket [168] and by F. L. Slocum. [169]

A. M. Fairlie [170] describes in detail the carbide installation at the enormous U.S. Government nitrate works at Muscle Shoals. There were twelve furnaces, each of capacity of 50 tons per 24-hour day the whole product (CaC_2 82·3, CaO 14·7%) being converted into cyanamide. The whole paper is of great interest. The carbide furnaces at Knapsack, Rhine Province, have been described by Allmand and Williams [171]

The *Canadian Chemical Journal* devotes one of its numbers to the Shawinigan electro-chemical industries, which indeed form one of the romances of the war. J. C. King [172] deals with the production of

[161] *J. Ind. Eng. Chem.*, 1919, **11**, 64.
[162] *Chem. and Met. Eng.*, 1919, **21**, 11.
[163] *Elect. Rev.* (Chicago), 1919, **74**, 814.　　[164] *J. Four Elect.*, 1919, **28**, 31.
[165] S. B. Wright, *Trans. Can. Min. Inst.*, 1918, **21**, 272 ; *J.*, 1919, 326A.
[166] *J. Four Elect.*, 1919, **28**, 115.
[167] Eng. Pats. 133098-133100 ; *J.*, 1919, 900A.
[168] Union Carbide Co., U.S. Pats. 1292386-7 ; *J.*, 1919, 286A ; 1310465 ; *J.*, 1919, 631A.
[169] Eng. Pats. 133101-133103 ; *J.*, 1919, 900A.
[170] *Chem. and Met. Eng.*, 1919, **20**, 8.　　[171] *J.*, 1919, 303B.
[172] *Canadian Chem. J.*, 1919, **3**, 262.

carbide by the Canada Carbide Co. The Willson rights were acquired in 1911. and larger 3-phase furnaces were worked out and installed in 1916, taking 8250 kv a. The total capacity of the two works of the company is 200 tons per day. The power used is 20 times what it was 20 years back- -the output is 40 times as great. Other papers by M. J. Marshall [173] and H W Matheson [174] deal with achievements and possibilities in the direction of pure organic products synthesised from acetylene. Enough has already been done to show that another and very important outlet for carbide has been secured Similar work was carried out at the Swiss factory at Lonza during the war The aldehyde resulting from the condensation of the acetylene was not only oxidised to acetic acid, but also reduced to alcohol 1 kilo. of alcohol required, however, more than 2 kilos of carbide Alcohol was also made from carbide in Sweden by the Sverre Uthenn process, and acetic acid was made in this country.

Mention should be made of a method proposed for the extraction of alkali from alkaliferous minerals, e g. felspar. The mineral, mixed with lime, is first preheated to 900° C. to expel water and carbonic acid and then fed into an electric furnace. Here it is subjected to a temperature of 1450° C. by means of resistors of graphite or carbon which pass longitudinally through the furnace, and with which the charge is in contact. Sintering occurs and the alkali volatilises and is collected on the roof of the furnace. The clinker, utilised for cement, is discharged by tilting. [175]

NITROGEN FIXATION BY ELECTRIC DISCHARGE IN GASES.

E. Briner and P. Naville [176] have carried out further experiments on the formation of nitrogen oxides in arcs. working with gases at low pressures. The matter is a complex one, as the yields per kw.h. depend on the nature of the electrodes and the composition of the mixture. A distinct improvement was, however, noted as compared with atmospheric pressure. With electrodes of Pt, Ir, and Cu, an excess of nitrogen was best The 50% $N_2 O_2$ mixture gave better results using electrodes of iron or nickel.

Several new furnaces have been proposed for this reaction. F. H. A. Wielgolaski [177] for example introduces the gases through tangential slit-like openings along the wall of the vertical arc chamber, and withdraws them through a restricted outlet in one of the electrodes which is hollow. By this means an excess pressure is maintained in the arc chamber. J. S. Island [178] strikes an arc between an inner rotating and

[173] Canadian Chem. J., 1919, 3, 254.   [174] Ibid., 3, 258 ; J., 1919, 793A.
[175] Eng. Pat. 117460; J., 1919, 255A.
[176] Helv. Chim. Acta, 1919, 2, 348; J, 1919, 814A.
[177] U.S. Pat. 1287807 ; J., 1919, 150A.
[178] U.S. Pat. 1316445; J., 1919, 819A.

an outer ring electrode. The air, blown in between these, produces a double-walled tubular arc of great surface. H. Andriessens,[179] in an interesting paper, criticises the Birkeland arc, which is only *optically* a sheet of 'flame. In reality, the air is being subjected, during the greater part of the time, not to the temperature of the arc, but to a lower temperature, which is, however, amply sufficient to decompose the oxides already formed. By combining an alternating high-tension discharge, passing between two electrodes close together, between which air is blown, with a strong direct-current magnetic field, he claims to get a helical arc of small surface and high power, with consequent better yields. He has worked up to a 50 60 kw scale.

Mention should be made of a patent by R. Pearson and H. C. Parkes.[180] They combine the electric discharge with the simultaneous action of a catalyst heated to 300° C. or more, and claim an increased yield of nitric acid. A. Classen [181] has a similar arrangement for the synthesis of ammonia in the electric discharge

This last reaction has been the subject of several papers E. Briner and A. Baerfuss [182] have made a careful study of the effects of composition of the initial mixture, pressure, nature and distance apart of the electrodes, and intensity of current and voltage. With platinum electrodes, the yield per kw.h. increases with decrease of pressure even more markedly than is the case for the synthesis of nitric oxide and an excess of nitrogen is favourable. With iron or nickel electrodes, neither of these effects is noticed. The maximum NH_3 concentration reached was 0·7% by volume, and the maximum energy yield 10 grms. per kw.h. E. B. Maxted [183] publishes a confirmation of his previous results, showing the formation of concentrations of up to 2% NH_3 A patent [184] also stands to his name, in which the mixed gases (1 N_2 : 3 H_2) are passed through an arc at 2000 C or higher under a pressure of 50 100 atmospheres, and suddenly cooled without loss of pressure, the residue free from ammonia again going to the heating chamber.

E. Briner [185] criticises Maxted's explanation of the formation of ammonia in the arc as involving an unjustifiable extrapolation of a thermo-dynamic formula of Haber. He argues strongly in favour of the view that the formation of ammonia, as of nitric oxide, under these conditions is due to a preliminary dissociation of the molecules concerned into atoms, the mass action law therefore not being applicable

[179] *Z. Elektrochem.*, 1919, **25**, 255; *J.*, 1919, 814A.
[180] Eng. Pat. 130693; *J.*, 1919, 718A.
[181] Norw. Pat. 28990; *Chem. Abs.*, 1919, **13**, 403.
[182] *Helv. Chim. Acta*, 1919, **2**, 95; *J.*, 1919, 219A.
[183] *Chem. Soc. Trans.*, 1919, **115**, 113; *J.*, 1919, 219A.
[184] Eng. Pat. 130023; *J.*, 1919, 680A.
[185] *Helv. Chim. Acta*, 1919, **2**, 162; *J.*, 1919, 284A.

in the ordinary form given it. There is much to be said for his view.

The same author and Baerfuss have also published a study of the production of hydrocyanic acid in the arc at low pressures from nitrogen and methane.[186] Working with a mixture of composition $1CH_4 : 5N_2$, at a pressure of 100 mm., and an arc tension of 500 volts, they get a gas containing 0·75% HCN by volume and a yield of 7·4 grms. HCN and 0·5 grm. NH_3 per kw h. The reduced pressure avoids all deposition of soot on the electrodes.

NITRIDES, CYANIDES, AND CYANAMIDE

The Armour Fertiliser Works have patents [187] dealing with the formation of aluminium nitride. A mechanical mixture of briquettes (consisting of alumina, carbon, and a binder) and infusible resistance elements is charged into the top end of a furnace, and meets an ascending current of nitrogen. In the furnace the charge is heated by a current passing between the conducting walls and a central electrode or electrodes As both nitrogen and solid charge are cold when they enter the furnace, the bulk of the current flows across the middle of the furnace, after preheating has taken place With more than one central electrode, polyphase current is used The charge is maintained at 1800 2000° C. for 3 4 hours.

A. R Lindblad [188] describes furnaces for the production of nitrides, e.g. of silicon. In one form, a shaft furnace is used, the charge entering at the top and the nitrogeneous gases being drawn downwards through the charge by means of an outlet pipe near the base. One electrode is suspended in the charge, another enters through the bottom of the furnace. The product is raked out at the bottom In another type, an open shaft furnace is used, one electrode is suspended in the middle, and the furnace lining forms the other Nitrogeneous gases are introduced below, and the waste gases escape at the top. A third form is closed, and has free spaces between the charge and the walls. The electrodes all pass through entrances in the walls Nitrogen is introduced at the bottom or through the electrode ports.

The American Cyanamid Co. fuses a mixture of salt and crude cyanamide in the electric furnace. The melt is tapped, and rapidly chilled below redness. The product contains more than 30% NaCN, together with lime, calcium chloride, and salt [189] R Hara and R. Hayashi [190] have carried out an investigation on the Bucher reaction. A mixture of soda ash, carbon, and iron, in the proportions 1 . 0·7 : 1 was heated in nitrogen in a vertical electric tube furnace at 950° C.

[186] Helv. Chim. Acta, 1919, 2, 663; J , 1920, 105A
[187] Eng. Pat. 122829 and U S Pats. 1317327-8; J., 1919, 912A.
[188] Eng. Pats. 119243 and 122523 ; J., 1919, 681A, 175A.
[189] U.S. Pat. 1282405; J , 1919, 41A.
[190] J. Chem. Ind. Tokyo, 1919, 22, 175; J., 1919, 628A.

for 90 minutes. An 80% conversion to cyanide resulted. Presence
of silica diminished the yield. Traces of chloride and of sulphate were
without effect. C. B. Jacobs [191] produces cyanide by the interaction
of nitrogen with an intimate mixture of carbon and " nascent " alkali
metal resulting from the electrolysis of an alkali compound.

There should finally be mentioned an account by A. M. Fairlie [192]
of the electrothermal cyanamide plant at Muscle Shoals, which gives
us, for the first time to the writer's knowledge, full details of such a
plant and its operation. Altogether there are 1536 furnaces, each of
which can run through a charge of 1600 lb. of carbide in something over
40 hours, giving a product with 63% cyanamide.

ELECTRICAL SEPARATION OF DUST AND FUMES.

The Cottrell method of electrostatic separation of fumes, surely one
of the biggest technical advances of the last decade, continues to find
further application. In fact it is difficult to imagine any problem of
the kind which it is incapable of solving, so great is its flexibility.

Attention may first of all be drawn to two papers of general interest
by H. D. Braley [193] and by E. E. Thum.[194] The latter discusses many
points of importance in its application to smelting operations. Its
use has been described during the last year for settling tar fog,[195]
dust from blast furnace gases,[196] and fumes from a silver refinery.[197]
In the first case it was found to be efficient at high temperatures, where
other methods failed, the settling was generally more complete; the
aqueous condensates subsequently obtained were cleaner, and by com-
bining its action with progressive temperature lowering, a fractional
precipitation became possible. In the second case again, clean dry
hot gas was produced for hot stoves and boilers, there was a large
recovery of water-soluble potash compounds, and the fluxing of stove
bricks was avoided. The last paper gives a detailed account of the
plant of the United States Metals Refining Co. at Chrome, N.J. A
100% efficiency is there obtained. J. M. Wauchope [198] describes its
application, with stress laid on the electrical details, to smelter gases.
There is a fair number of new patents The Research Corporation
(with L. Bradley, C. E. Murrell, and C. W. J. Hedberg) suggest an
apparatus in which the flow of gas is regulated by means of a constric-
tion at the entrance or exit of the duct which acts as the collecting

[191] U.S. Pat. 1311231. J., 1919, 681A

[192] Chem. and Met. Eng., 1919, 20, 13

[193] Chem. and Met. Eng., 1919, 20, 384.

[194] Chem. and Met. Eng., 1919, 20, 59. J., 1919. 163A.

[195] J. G. Davidson, Trans. Can. Min. Inst., 1918. 21, 252; J., 1919, 315A.

[196] W. H. Gellert, Blast Furnace and Steel Plant, 1919, 7, 334; J., 1919, 637A.

[197] W. G. Smith and A. A. Heimrod, Chem. and Met. Eng., 1919, 21, 360; J. 1919, 864A.   [198] Elect. Rev. (Chicago), 1919, 74, 744.

electrode, thereby producing an increased frictional resistance.[199]
To eliminate fluctuations in gas velocities caused by temperature
differences, the gases are made to pass in a downward direction.[200]
Water vapour is added to maintain the conductivity of the gases.[201]
By the injection of suitable gases, fumes can be produced in gases from
which it is otherwise difficult to remove the constituent desired, and
these fumes can be precipitated electrostatically by circulating the
gases through a closed system[202]; e.g., ammonium bisulphite by
injecting ammonia into smelter gases, potassium chloride by adding
hydrochloric acid to cement-kiln or blast-furnace gases, ammonium
bromide by injecting ammonia into gases containing bromine.   Pyrites
burner gases can be freed from dust above the temperature at which
sulphuric acid will condense.   The latter can be removed by a second
precipitation after cooling[203]   By surrounding a discharge electrode
with a vertically arranged series of receiving chambers, and collecting
the contents of these separately, a fume can be graded[204]   The Inter
national Precipitation Company (with W A. Schmidt and H V. Welch)
have another series of patents   Coarser particles are first settled by
gravity, the finer ones by electrostatic separation[205]   The collecting
electrode is porous, e.g. of terra-cotta, and water is supplied from the
outer to the inner surface[206]   In mixtures containing oxides of sulphur
and nitrogen, together with water vapour, the reaction can be acceler
ated by passing the gases through successive fields of the right intensity
and the nitrosyl-sulphuric acid mixture precipitated electrostatically.[207]
Sulphur trioxide formed catalytically can be sprayed with water, and
the sulphuric acid precipitated electrostatically.[208]   Sulphuric acid
can be separated similarly from the products of the interaction of sul
phur dioxide, chlorine, and water vapour[209]

   J. N. Carothers and W H Ross recover phosphoric acid from fumes
involved in smelting operations, condensing above 100 C[210]   S. F.
Barclay designs his apparatus so that the particles are carried in the
direction of movement of the gases, and collects them on a plate
sprayed with water, through which the gases pass.[211]   In another

[199] Eng. Pats. 107389 and 120573 ; J., 1919. 61A, 97A.
[200] Eng. Pat. 119238 ; J., 1919, 61A.
[201] Eng Pat. 119236 , J., 1919, 61A.
[202] U.S. Pats. 1291745 and 1292016 ; J , 1919, 490A. 286A.
[203] U.S. Pat. 1284175 , J , 1919, 74A
[204] U S. Pat. 1297159 ; J , 1919, 397A.
[205] U.S. Pat. 1298409 ; J., 1919, 397A
[206] U.S. Pat. 1309221 ; J., 1919, 645A
[207] U.S. Pat. 1284166 ; J., 1919, 73A.
[208] U.S. Pat. 1284167 ; J., 1919, 73A
[209] U.S. Pat. 1285856 ; J., 1919. 133A   See also U.S. Pat 1307930 , J ,
1919, 587A.
[210] U.S. Pat. 1283398 ; J., 1919, 75A.
[211] Eng. Pat. 125681 ; J., 1919, 397A.

patent, an electrically conducting deposit and a good corona discharge
are ensured by adding a conducting dust to the gases.[212]   In yet
another, the gas pressure is adjusted to the voltage employed, being
lower, the higher the latter.[213]   F. Schultz employs an apparatus in
which the discharge electrode consists of a number of short, horizon-
tally arranged tubes, suspended in the outer vertical tubular collecting
electrode.   The dielectric constant of the insulating material of the
discharge electrode is greater than that of the material of the outer
electrode.[214]

Mention may finally be made of a small testing apparatus for the
electrostatic analysis of smokes.   Reference must be made to the
original [215] for details.

ELECTRICAL SEPARATION OF COLLOIDS AND EMULSIONS.
ELECTRO-OSMOSIS.

There are several patents describing apparatus for the separation of
oil-water emulsions and the drying of oils.   They do not appear to
contain any striking features, and this reference must suffice   An
article has appeared [216] describing the processes and apparatus of
Osmosis, Ltd., with particular reference to the grading and purifying
of clays, electrical filtration, and the preparation of pure gelatin and of
alumina and silica sols.

[212] Huntington, Heberlein and Co., Ltd., and others, Eng. Pat. 127119, *J.*, 1919, 521A.
[213] Ger. Pat. 311144; *J.*, 1919, 451A.
[214] Ger. Pat. 312049; *J.*, 1919, 752A.
[215] R. C. Tolman and others, *J. Amer. Chem. Soc.*, 1919, **41**, 587; *J.*, 1919, 391A
[216] *Chem. Trade J.*, 1919, **65**, 306.

OILS, FATS, AND WAXES.

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The events of the past few years must have brought home to everyone the vital importance to our national well being of an adequate supply of oils and fats, both for edible and technical purposes. This has been exemplified by the frantic search in the mid European Empires for new home-grown sources of oils, such unpromising materials as horse chestnut and beech nuts being pressed into service.

Of great importance also to the agricultural interests and so to the community at large is the supply of oil cake. Whether it is possible to increase the supply of raw material in our markets for these industries by artificial means such as export duties levied in certain localities on palm kernels exported to places outside the British Empire is a debatable point. A glance however at the recent enormous issues of new capital by the seed-crushing soap and margarine manufacturing companies shows at least that this country is fully alive to the possibilities opened up in these fields.

The edible oil-refining and margarine-making industries in particular have attained large proportions during the last few years and bid fair to give this country a pre-eminent position in the supply of these products.

Since there is no immediate likelihood of any great increase in the production of animal fats, especially of butter fat, the need for margarine is bound to become greater, and it will be necessary to ensure a larger supply of the raw materials either by increasing the production of the oils already used or by bringing in other oils which have hitherto been used only for technical purposes.

The method of hydrogenating oils has done this to a large extent, and the amount of solid fat prepared in this country by this process must have reached an enormous total, although no statistics are available.

A recent proposal to use hardened castor oil must be looked upon with misgiving, as in order to destroy the physiological action of castor oil

it is necessary to carry the process of hydrogenation to completion and then the resulting tristearin or trihydroxystearin as the case may be will be far too hard to be easily assimilated.

The late insistent need for glycerin has resulted in the development of a commercial process for the manufacture of synthetic glycerin. Eoff, Linder, and Beyer in the United States and Connstein and Lüdecke in Germany, working along similar lines, have obtained yields of over 20% of glycerol by the fermentation of sugar

The prospect of cheaper glycerin is turning attention to the possibility of converting the free fatty acids in an oil into their glycerides, thus doing away with the costly and wasteful process of removing them in the refining of edible fats. Some experiments made by the writer in 1909 demonstrated the possibility of this reaction although as the contact substance used was the Twitchell reagent the product was obviously unsuitable for food   More recently it has been proposed to use certain metallic oxides like thorium oxide and titanium oxide as catalysts.

The rapid development of aircraft during the last few years has called for an increasing supply of castor oil for lubricating purposes   This need is not likely to diminish much in the future, and it is to be hoped that this country keeps the supply in its own hands   The estimated amount used in 1917 was upwards of 6 million gallons

Deficiency of transport probably explains why Indian exports of castor seed decreased from 120,191 tons in 1911 12 to 86,100 tons in 1917 18. True, the exports of oil had increased, but in nothing like the same proportion   Best quality oils of the first or second expression are demanded by the aircraft engineers as will be seen from the following figures issued by the United States War Department : " The castor oil should be colourless and have the density of 0·959 0·968 at 60° F. It should be completely soluble in 4 volumes of alcohol of the sp. gr. 0·831 at 60° F. The free acids should not exceed 1·5% calculated as oleic acid   The saponification value shall fall within the limits 176 to 187 and the iodine value 80 to 90   The unsaponifiable matter shall not exceed 1% and the viscosity in a Saybolt apparatus is given as 450 seconds at 130° F., and 95 seconds at 212° F., and the flash point determined in a Cleveland open cup 450° F. The freezing point shall be below zero F. Cottonseed oil, rosin oil, and rosin must be absent."

The acetyl value ought certainly to have been included as the above given figures would permit the admixture of a small amount of thickened rape oil.[1]

There has not been a large amount of new work on oils and fats published during the past year, but there are signs indicating that we may look forward to an increase in the work in the near future.

[1] J., 1919, 20B.

I. S. Falk [2] has continued his exhaustive investigation on the action of enzymes on glycerides and finds that calcium chloride inhibits the hydrolysis of olive oil This is rather surprising inasmuch as sodium chloride has a very slight if any retarding effect whilst manganous sulphate has a positive accelerating effect. In this connection may be noted the work of O. Fernandez,[3] who shows the presence of proteolytic enzymes in poppy seed, almonds, filberts, arachis nuts, hemp seed, walnut, and castor seed.

As an instance of the rapidity with which hydrolysis takes place in palm oil some figures are given by Balland,[4] who shows that in two samples the free fatty acids had increased from 8·3% to 61·2% These oils must either have been kept badly, that is exposed to light and moisture, or have contained an unusual amount of the organic matter from the pericarp of the fruit, as the present writer has kept ordinary commercial palm oil for nine or ten months without the free fatty acids increasing by more than 4 or 5%, say from 13 to 18%

Possibly as the oils mentioned by Balland were " chop " oils intended for food for the African troops in France they had been prepared at a temperature too low to sterilise the hydrolytic enzymes If the fruits are gathered before they are quite ripe and heated in water the enzymes are killed and oils can be expressed containing only 0·2% free fatty acids and which keep quite well [5] This is borne out by some experiments of H A Gardner,[6] who finds that the hydrolysis of oils is prevented to a large extent by heating them for a short time to 105° C. and subsequently filtering

L. Ubbelohde and W Roederer [7] have compared the activities of Twitchell's reagent prepared from oleic acid, castor oil castor oil fatty acids, and hydrogenated castor oil and its fatty acids. They find no difference in the rate at which hydrolysis proceeds or in the total amount of free fatty acids formed between the various reagents.

The colour of the resultant fatty acids is considerably lighter when the reagent is prepared with hydrogenated castor oil or its fatty acids. When this reagent has been used the glycerin water is also lighter in colour and easier to purify.

P. Bertolo [8] advocates the treatment of oils with small amounts of sulphuric acid of sp gr. 1 7 in order to remove the impurities from oils and fats before they are hydrolysed with Twitchell's reagent. He also states that the amount of reagent has no influence

[2] J Biol. Chem., 1918, 36, 229 ; J., 1918, 741a.
[3] Anal. Fis. Quim., 1918, 16, 728 ; J., 1919, 329a
[4] Comptes rend , 1918, 167, 673 ; J., 1918, 774a.
[5] P. Ammann, Dépeche Col., 1919 ; J., 1919, 166b.
[6] J. Ind. Eng. Chem., 1919, 11, 759 ; J., 1919, 912a.
[7] Seifenfabr., 1918, 38, 425, 449, 475 ; J., 1919, 425a.
[8] Annali Chim. Appl., 1919, 12, 27 ; J., 1919, 831a.

on the speed of hydrolysis or on the extent to which the hydrolysis will take place. This is contrary to the experience of the present writer, who has always found that by increasing the amount of the reagent up to about 5% it is possible to obtain a material reduction in the time required.

The investigation undertaken by H. L. White [9] in an attempt to discover the conditions which govern the formation of the glycerides of unsaturated fatty acids during the growth of the plant has yielded negative results. It was found that by varying the conditions under which the plant grew to maturity in most cases no difference could be detected in the oil, while in a few cases only a very slight reduction had taken place in the iodine value of the extracted oil. Enzymes were found to cause hydrolysis of the glyceride without affecting the degree of unsaturation of the fatty acids.

In the opinion of the present writer the most promising field for research in this direction lies in the method of selective breeding This method has been used successfully in increasing the oil content of various seeds.

A new method for removing the free fatty acids from oils and fats patented by H. Fremerey [10] consists in saturating the oil with dry ammonia gas at a temperature as low as is consistent with keeping the oil in a liquid condition. The ammonium soaps are precipitated in colloidal form by the addition of small amounts of water and separated by filtration. The ammonia can be subsequently recovered. This does not seem very promising for use on a large scale, and is hardly likely to replace the well-known method of de-acidifying oils and fats by means of a fixed alkali or alkaline-earth.

A patented process for removing small amounts of metallic impurities from oils and fats [11] involves the agitation of the warm fat with an aqueous solution of a lower aliphatic acid, preferably a dibasic acid or one containing a hydroxyl or amino group. The examples given are oxalic, lactic, tartaric, and glycollic acids and glycocoll. This seems a somewhat expensive method and does not offer any outstanding advantages over the simpler process of boiling with a dilute mineral acid.

A new use for lead oleate is reported from the United States, where it has been used successfully to prevent tackiness in manufacturing rubber goods. The consumption for this purpose is said to reach 1 million pounds per annum.

A mechanical method for separating the bulk of emulsified wool grease from the soap sud resulting from the scouring of wool has been patented by W. Kelsey. [12] The separation of wool grease by mechanical

[9] *J. Ind. Eng. Chem.*, 1919, **11**, 648 : *J.*, 1919, 588A.
[10] Ger. Pat. 312136; *J.*, 1919, 781A.
[11] Elektro-Osmose A.-G., Ger. Pat. 309157; *J.*, 1919, 832A.
[12] Eng. Pat. 123848; *J.*, 1919, 282A.

means deserves more attention than it gets in this country. A far lighter wool grease and one much more suitable for the manufacture of lanolin is prepared by these methods than is done by the old wasteful Yorkshire method of cracking the suds with a mineral acid and pressing the precipitated cake of suint through sacking

C. H. Wright [13] has extended his work on specific gravities to the determination of the refractive index with the object of finding a formula whereby the refractive index may be calculated for any temperature. As a result of his calculation the following formula is deduced for converting the refractive index at any temperature, t, to the refractive index at 40° C. :

$$n_{40} = (n-1) \cdot \frac{0.9696}{1 - 0.00076t} + 1.$$

Since from the table given the difference between the calculated and determined figures is least when the determination is made at a temperature close to the one desired, the author recommends to determine the refractive index at a temperature as near to 40° as it is possible to obtain easily and calculate the result by his formula to 40° C. In order to show the usefulness of this formula the author gives some figures obtained by different observers at various temperatures calculated to a common temperature Thus for linseed oil $n_{16}\ 1.4835 = n_{40}\ 1.4742 : n_{20}\ 1.4800\ n_{40}\ 1.4725 : n_{20}\ 1.4812\ n_{40}\ 1.4737 ; n_{60}\ 1.4660 = n_{40}\ 1.4734$, and for almond oil $n_{15.5}\ 1.4728\ n_{40}\ 1.4639 : n_{20}1.4701 = n_{40}\ 1.4628 , n_{20}\ 1.4712 = n_{40}\ 1.4639 ; n_{60}\ 1.4555\ n_{40}1.4627.$ These values are in good agreement A discrepancy is noticed in the numbers given for turtle oil.

The extraction of oils from fruits and kernels rich in oil by means of a centrifugal extractor is coming more into favour as it is considerably more rapid than the use of an hydraulic press.

A process patented by H. R. Greenhalgh [14] consists in first heating the fruit (palm fruit) in a jacketed kettle. and then centrifuging to remove the bulk of the oil It is usually necessary. as indeed the patentee states, to submit the residual pulp to pressure in an hydraulic press in order to remove the last traces of oil.

The trend of development in modern plant is towards continuous working. This principle has been applied to the extraction of oils from nuts, etc., by means of solvents by A. McC. Winters,[15] who uses a series of three superimposed extraction vessels. The material to be extracted is passed downwards from one vessel to another aided by a screw conveyer.

A curious method of assisting the separation of " stearine " from

[13] J., 1919, 392T.   [14] Eng. Pat. 111676; J., 1918, 741A.
[15] Eng. Pat. 120156; J., 1918, 774A.

" oleine " from coconut oil has been patented by W. P. Shuck,[16] who adds to the oil before hydrolysing 5% of flax or other fibrous material. It is claimed that by this means the oil is easier to press and yields a much larger proportion of liquid glycerides.

MARINE ANIMAL OILS.

Oils having remarkably high iodine values have been obtained by M. Tsujimoto [17] from the livers of various species of shark found in Japanese waters.   One oil prepared from the liver of *Pristiurus pilosus* showed the following characteristics :   sp. gr. at 15°/4° C. 0·8664, saponification value 28·2, iodine value 309·0, n_D^{20} 1·4912, unsaponifiable matter 85·5%, acid value 0·32, insoluble bromides from fatty acids 7·0%.   The oil was found to contain 79% of the hydrocarbon squalene. Presumably the other 6·5% of unsaponifiable matter consisted of alcohols, but no information has yet appeared as to the amount of cholesterol in this oil.

Since the amount of insoluble bromides from the fatty acids is only 7% the oil can only have contained a small amount of clupanodonic acid, the high iodine value being solely due to the presence of the highly unsaturated hydrocarbon squalene, which seems a characteristic component of the oils from the livers of Japanese sharks.   It is worthy of note that no squalene could be detected in the oils from the livers of five species of Japanese ray examined by the same author.

A research undertaken by H. S. Bailey and J. M. Johnson,[18] in an endeavour to determine by the analysis of the oil from tinned salmon the species of fish from which it has been derived, has yielded promising results.   They rely on differences in the iodine value and in the percentage of insoluble bromides miscalled in the paper hexabromide value.

Since clupanodonic acid is a characteristic of fish oils it is preferable to describe the ether-insoluble bromides correctly as octobromides or merely insoluble bromides.   It would also be well to state that the figure for the insoluble bromides refers to the glycerides or to the fatty acids.   In the paper under discussion the figures refer to the glycerides.

The present writer is strongly of the opinion that the fatty acids should be used in all cases for the determination of the insoluble bromides, especially in the case of fish oils containing glycerides which yield bromides extremely difficult to wash.   No danger of oxidation of the fatty acids during their preparation is to be apprehended if proper precautions are observed.

Authenticated specimens of various species of salmon have been examined with the following results :

[16] U.S. Pat. 1288228 ; *J.,* 1919, 186A.
[17] *J. Chem. Ind. Tokyo,* 1918, 21, 1015 ; *J.,* 1919, 109A.
[18] *J. Ind. Eng. Chem.,* 1918, 10, 999 ; *J.,* 1919, 51A.

Variety.	Iodine value.	Insoluble bromide value, %.
Alaska red. Sockeye (*Oncorhyncus nerka*)	140·72 118·10	32·61 37·35
Chinook (*O. tschawytscha*) . .	126·62 131·48	23·86 31·06
Silverside. Medium Red Coho (*O. Kisutch*) . . .	155·61 166·40	45·98 59·31
Chum (*O. Keta*) . . .	133·10 136·19	27·59 30·12
Steelhead . . .	141·90	36·22

The figures obtained for oils which have been extracted from fresh salmon by means of ether show unaccountable variations, as will be seen from the following table :

Variety.	Iodine value	Insoluble bromide value, %.
Chinook	139·49	26·83
,, ...	67·08	-
Silver	75·99	0·41
Chum	112·22	2·36
,, ...	71·68	---

As a considerable time elapsed between the oils being extracted and their examination one can only suppose that oxidation has taken place.

DRYING OILS.

Some highly interesting experiments in an attempt to render this country independent of foreign supplies of linseed have been made by the British Flax and Hemp Growers' Association.[19] Their results show that an oil having superior drying powers to that obtained from foreign-grown seed can be produced. They also give a rosy account of the financial aspect of the question, but do not say whether their estimates are based upon post-war conditions.

A drying oil derived from a species of *Hyptis spicigera*[20] (Lamarck), known locally as " benefing " oil, has been suggested as a substitute for linseed oil. The plant grows in profusion in the Niger and Senegal districts, and also in Madagascar. In the latter place the oil is stated to be used for edible purposes.

Some figures for an extracted oil published by M. E. Milliau show that the oil has a specific gravity of 0·9436 and an iodine value of 171

[19] *J.*, 1919, 65R.
[20] *Bull. de l'Office Coloniale*, 1918, 11, 345 ; *J.*, 1919, 426A.

If the oil dries to a clean hard film and the seed can be easily collected in sufficient quantity there should be a commercial future for them.

The oil from Para rubber seed, *Hevea Braziliensis*, has been examined by A. Dubosc,[21] who states that seed containing 52% of oil yielded 33% in a single pressing. He is evidently referring to decorticated seed, since B. J. Eaton (see below) obtained only 19·3% of oil from the whole seed by extraction with a volatile solvent.

Dubosc records the iodine value of 130·8 and states that the oil yielded a good rubber substitute when vulcanised either hot or cold. The extraction of Para rubber seed obtained from Malay carried out by B. J. Eaton [22] on a commercial scale yielded · Oil 19·3%, foots 2·93%, meal 76·6%, loss 1·7%. From these figures and present-day values he concludes that it would not be remunerative to import nuts into this country and work them up for the production of oil. The cost of shipping given in his estimate, namely £15 10s. per ton, ought to be reduced in the near future. Moreover, this charge could be reduced by approximately half if the seeds were decorticated before shipping since the shell comprises 45% of the whole seed. The author estimates that a yield of 26,000 tons per annum of oil could be obtained from the seed grown in the Malay Peninsula

The following figures are recorded for the oil extracted by means of a volatile solvent : Sp. gr at 15·5 ` C 0·9245, free fatty acids as oleic acid 16·9%, saponification value 192·5, iodine value 139·3. The oil is stated to have poor drying properties. This is undoubtedly due in part in this particular sample to the large amount of free fatty acids. It is, however, an excellent substitute for linseed oil as a basis for the manufacture of soft soap.

Candlenut oil from *Aleurites triloba* has been examined by Lespinasse[23] who found the following characteristics : Sp. gr. at 15 ` C. 0·927, free fatty acids as oleic acid 0·7%, saponification value 175, iodine value 137. The oil is eminently suitable for the manufacture of soft soap, and since it possesses pronounced drying properties it could be used to replace linseed oil in the manufacture of paint and linoleum.

The seeds from three species of East African manihot have been examined by C. Grimme [24] who records the following figures :

[21] *Caoutchouc et Gutta Percha*, 1919, 9785 ; *J.*, 1919, 544A.

[22] *Agric. Bull. Fed. Malay States*, 1919, **12**, 73 ; *J.*, 1919, 729A.

[23] *Ann. Falsif.*, 1919, **7**, 152 ; *J.*, 1919, 687A.

[24] *Chem.-Zeit.*, 1919, **43**, 505 ; *J.*, 1919, 831A

Oil	Yield of oil	Sp. gr. at 15 C	n_D^{40}	Acid value	Sapon. value	Iodine value	Reichert Meissl value	Unsap. matter, %
M. Glaziovii								
seeds	11.06	0.9235	1.4674	1.68	187.5	142.0	0.35	0.76
kernels	41.34							-
M. dichotoma								
seeds	14.65	0.9265	1.4661	1.36	188.6	133.1	0.51	0.81
kernels	46.11							
M. piauhyensis								
seeds	12.61	0.9225	1.4681	1.49	187.7	144.0	0.42	0.78
kernels	48.95							
Commercial		0.9245	1.4667	3.74	188.1	136.0	0.47	1.09

FATTY ACIDS

Oil.	n_D^{40}	m. pt. °C	Solidif. pt. °C	Iodine value	Neutralisation value	Mean molecular weight
M. Glaziovii	1.4575	23	21.5	144.1	188.7	297.5
M. dichotoma	1.4549	23.5	22	133.8	189.9	295.6
M. piauhyensis	1.4576	21	20	145.3	188.3	298.3
Commercial	1.4563	22.5	20.6	138.1	189.3	296.6

H. E. Wunschendorff [25] has obtained a yield of 5% of a drying oil from the seeds of fenugreek. The oil had sp. gr. at 15 C 0.9471, n_D^{22} 1.4774, saponification value 189.5, iodine value 137.8, free fatty acids 3.2%, insoluble fatty acids 92.9%, volatile acids 1.50%, unsaponifiable matter 0.90%, phosphatides 6.25%, phytosterol 0.55%, melting at 135.5 C, and yielding an acetate melting at 131 C.

The amount of phosphatides is extremely large and further research would be welcome in order to show their relationship to egg yolk lecithin.

The oils from the seeds of two species of dogwood tree, *Cornus sanguinea* and *C. stolonifera*, have been examined by W. Normann,[26] who gives the following figures:

	Cornus sanguinea				*Cornus stolonifera*
	Oil from pulp		Oil from kernel		
Yield of oil	30.7 - 35.3%		8.76	12.26%	21.23%
Acid value	4.2	37.5	2.5	108	7.8
Saponification value	192	194	193	197	197
Iodine value	115.5 - 195.4		143.8	117.8	114.2
Unsaponifiable matter	1.65	2.9%	0.4	1.1 %	0.67%

The high iodine value given for the oil from the pulp must be accepted with reserve.

[25] *J. Pharm. Chim.*, 1919, 19, 397; *J.*, 1919, 588A.
[26] *Chem. Umschau*, 1918, 25, 49; *J.*, 1919, 426A.

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The examination of the oil obtained from the seeds of the prickly lettuce, *Lactuca scariola oleifera*, has been undertaken by E. Griffith Jones,[27] who states that the seeds of the plant, which is grown in Upper Egypt, are pressed locally in a primitive fashion and yield a golden-yellow oil having a pleasant taste. The oil, which forms between 33 and 37% of the weight of the seed, does not deposit stearin even on long standing at 0° C. The following characteristics were determined. Sp. gr. at 15·5°/15·5° C. 0·9247, n_D^{40} 1·4672, acid value 1·8, saponification value 190·0, Reichert Meissl value 0·1, titration number of insoluble volatile acids 0·2, iodine value 127·0, acetyl value 12·0. The oil dried to a hard film after 5 days' exposure and contained linolic acid. Linolenic acid could not be detected.

The seeds of the evening primrose, *Oenothera biennis*, contain 16·93% of a golden-yellow drying oil similar in taste and smell to poppy-seed oil. This has been examined by A. Heiduschka and K. Luft.[28] The oil is optically inactive and deposits a few crystals when cooled to 11° C. It showed the following characteristics: Sp. gr. at 15° C. 0·9283, n_D^{40} 1·4722, free fatty acids nil, saponification value 195·2, Reichert Meissl value 2·61, titration number of the insoluble volatile acids 0·57, iodine value 148·92, acetyl value 13·9. The definite Reichert-Meissl value is caused by the presence of caproic acid. By the bromination of the liquid fatty acids the authors isolated an ether-insoluble hexabromide melting with decomposition at 195–196° C. (ordinary hexabromolinolenic acid melts at 180°–181° C.) It is concluded therefore that the acid is γ-linolenic acid.

The composition of the liquid acids is given as γ-linolenic acid 2·50%, α-linolic 30·20%, β-linolic 38·41%, and oleic acid 29·19%. The γ-hexahydroxystearic acid obtained by oxidation with alkaline permanganate crystallised in minute needles melting at 245° C. with decomposition. The solid fatty acids consist mainly of palmitic acid, but indications were obtained of the presence of an acid of higher molecular weight.

SEMI-DRYING AND NON-DRYING OILS.

H. Nakatogawa[29] has recorded the following figures for the oil expressed from the seeds of *Amorpha fruticosa*, a leguminous plant indigenous to Manchuria. The seeds yielded 8·71% of a brownish-yellow oil having sp. gr. at 15·4° C. 0·9426, n_D^{20} 1·4845, saponification value 182·5, iodine value 133·71, acid value 7·06. The oil is stated to have slight drying properties and stands on the border line between the drying and semi-drying classes of oils. In view of the small yield of oil the seeds are not likely to be commercially profitable.

[27] *Rep. Pub. Health Lab. Cairo*; J., 1919, 226A.
[28] *Arch. Pharm.*, 1919, **257**, 33; J., 1919, 426A.
[29] *J. Chem. Ind. Tokyo*, 1918, 21, 865; J., 1919, 21A.

The following figures have been recorded by E. Cheel and A. R. Penfold [30] for the oil from the seeds of an Australian grown specimen of Mexican Buckeye, *Ungnadia speciosa* The seeds yielded to ether 50% of a pale yellow oil, sp. gr at 15 15 C 0·9117, n_D^{20} 1·46666, acid value 9·38, saponification value 203, iodine value 84, unsaponifiable matter 0·6% The insoluble fatty acids free from unsaponifiable matter had sp gr. at 30 15 C 0·8848, n_D^{20} 1·4607, m pt 26 C., neutralisation value 194·46, mean molecular weight 288·22, iodine value 87. Linolenic acid was absent and only traces of linolic acid could be detected by the bromide test The seeds contain a cyanogenetic glucoside.

S. Kobayashi [31] has determined the characteristics of the seed oils of the citron (*Citrus aurantium* L, sub sp *junos*), the Chinese citron (*C. aurantium* L., sub. sp. *sinensis*) and the kumquat (*Fortunella japonica*) and states that the oils contain about 19·27% of solid acids.

The oil obtained from prune kernels has been examined by L Fordyce and D M Torrance [32] The kernels yielded to ether 42% of an oil which on cooling to 5 C deposited one-third of its volume of "stearine" The "stearine" had sp gr 0·9055 and saponification value 239·8 The "oleine" had sp gr. 0·9199, saponification value 207·4. The "stearine" from its high saponification value probably contains a quantity of the glycerides of lauric acid and it would be interesting to know the Reichert-Meissl value and the titration number of the insoluble volatile acids

K Alpers [33] publishes the following figures for the kernel oils of some stone fruits :

Oil	Yield of oil	Sp gr	Butyro refractometer at 25 C	Saponification value.	Iodine Value
Plum kernel .	37·38%	0·9193 to 0·9213	65·1 to 66·7	188·1 to 198·5	103·6 to 121·1
Cherry kernel .	38·71%	0·9128 to 0·9247	74·7 to 77·3	192·1 to 197·8	111·6 to 122·6
Peach kernel .	45·45%	.	.	.	
Apricot kernel .	51·43%	.		.	--

Three samples of plum kernel oil examined by Utz,[34] one of known purity and two commercial samples, gave a positive coloration with Bieber's reagent, but failed to give a Baudouin reaction.

[30] *J.*, 1919, 74т.
[31] *J. Chem. Ind. Tokyo*, 1918, 21, 1235 ; *J.*, 1919, 294A.
[32] *Chem. News*, 1919, 118, 242 ; *J.*, 1919, 426A.
[33] *Z. Unters. Nahr. Genussm.*, 1917, 34, 433 ; *J.*, 1919, 729A.
[34] *Chem. Umschau*, 1919, 26, 49 ; *J.*, 1919, 505A.

Endeavours are being made to find a outlet for the silkworm chrysalides which are produced in quantities in Italy.

G. Tagliani states [35] that the chrysalides contain 30-40% of oil which he proposes as a basis for soaps or emulsions used in cotton and wool scouring. He also states that the dry residue can be used as a cattle food, a manure, or a fuel (briquettes).

The oil from beech nuts used in Germany during the war as an edible oil has been examined by W. Vaubel.[36] The kernels contain 43% of oil ; the specific gravity of the cold drawn oil varied between 0·9099 and 0·9169, and the refractive index varied between 1·4729 and 1·4732, all at 15° C The hot-pressed oil gave sp. gr. at 15° C. 0·920 0·9225, saponification value 191 196·3, iodine value 111·2 120. The oil becomes solid at -17° C., while the fatty acids melt at 24° C and solidify at 17° C. The press-cake it is stated sometimes contains a poisonous principle.

The seed of the American tomato examined by G Jamieson and H. S. Bailey [37] was found to contain 25% of oil and yielded 18%, when expressed. Nine samples of oil were examined and the following limiting values were obtained : Sp. gr. at 25° C 0·9181 0·9196, n_D^{25} 1·4715 1·4725, saponification value 187·0 192·0, iodine value 117·5 125·0, Reichert-Meissl value 0·1 0·3, titration number of the insoluble volatile acids 0·4 0·6, acetyl value 11·1 20·5, liquid fatty acids 76·1 80·6%, solid fatty acids 15·0 18·0%, The oil contained a small amount of arachidic acid.

Twelve samples of tsubaki oil from the islands of Izu have been examined by S Nakatogawa and S. Kobayashi,[38] who found the characteristics for the oils fell within the following limits : Sp. gr. at 15°/4° C. 0·9151 0·9161, refractive index 1·4685 1·4696, acid value 1·8 7·6, saponification value 190·3 192·6, iodine value 77·3 81·16. The oils gave a positive coloration in Bieber's test.

Ceratotheca sesamoides, a plant related to sesamé and growing on the Gold Coast (known locally as " bungu "), has been examined by E. R. Bolton.[39] The seeds yielded to petroleum ether 35·47% of a pale-yellow oil which deposited some " stearine " on standing. The following characteristics were recorded : Sp. gr. at 15° 15° C. 0·9163, butyro-refractometer at 40° C. 59·8, free fatty acids as oleic acid 0·63%, saponification value 190·2, iodine value 110·6, unsaponifiable matter 1·53%. Both the Baudouin and Halphen colour reaction gave negative results. The oil would make a good edible oil.

Sélé oil, used as an edible oil among the natives of the Belgian

[35] *Farber-Zeit.*, 1919, **30**, 65 ; *J.*, 1919, 377A.
[36] *Z. öffentl. Chem.*, 1919, **25**, 155 ; *J.*, 1919, 729A.
[37] *J. Ind. Eng. Chem.*, 1919, **11**, 850 ; *J.*, 1919, 781A.
[38] *J. Chem. Ind. Tokyo*, 1919, **22**, 435 ; *J.*, 1919, 871A.
[39] *Analyst*, 1919, **44**, 233 ; *J.*, 1919, 588A.

Congo, is stated [40] to consist of the glycerides of oleic, linolic, stearic palmitic, and lauric acids, also a small quantity of an acid of high molecular weight, probably arachidic acid or lignoceric acid. A similar oil is prepared from " Coconco," a variety of *Citrullus vulgaris*, bu in this case, owing to the fact that the nuts are difficult and expensive to decorticate and also to the comparatively low oil content of the kernels they are not likely to be exploited on a commercial scale.

Arachis oils of undoubted purity (from hand-shelled nuts) with a somewhat high saponification value have been noted by N Schlue and H. L. Maxwell, [41] who found the saponification values of 197 and 202 the iodine values being 94·5 and 95 respectively. These high values may possibly be due to a low proportion of arachidic acid.

The peculiar behaviour of a sample of castor oil from Egyptian-grown seed has been noted by W R G. Atkins. [42] The viscosity was abnormally low while the other characteristics were normal. Since the acetyl value was 149 the oil must have contained the normal amount of ricinoleic acid and the explanation of the abnormality of the oil seems to lie in the configuration of the fatty acids; possibly there exists an isomeric ricinoleic acid. Perhaps the determination of the optical activity would throw some light upon it.

It is stated, on the authority of H M Consul in Para, [43] that the brazil nut is being used as a source of salad oil As will be expected, it yields a very fine oil but the difficulty of decortication will most likely prevent its continued use. The same authority states that the press-cakes were used as fuel. Since the nut has a high protein value and is moreover highly palatable it could be used for human food as in biscuit making

SOLID FATS.

The sample of oiticica fat examined by C Grimme [44] differs considerably in its characteristics from that examined by E R. Bolton and C. Revis [45] Probably, as Grimme points out, the name oiticica is loosely applied to several members of the *Rosacea*, the oil for the most part being derived from *Pleuropyne umbusissuria*. Grimme records the following characteristics for the extracted fat · Sp gr at 15·5° C. 0·9158, n_D^{30} 1·4945, point of incipient fusion 15·9° C.; point of complete fusion 57° C., solidifying point 15·2 C. acid value 10·5, saponification value 195·3, iodine value 83·65, unsaponifiable matter 6·11%, m.pt. of fatty acids 63°-68° C The saponification value seems high considering the presence of such a large amount of unsaponifiable matter,

[40] J. Pieraerts, *Ann. Musée Colon Marseille*, 1916, **4**, ii . 1 ; *J.*, 1918, 741A.
[41] *Chem. News*, 1919, **119**, 185. *J*, 1919, 871A.
[42] *Analyst*, 1919, **44**, 287 ; *J.*, 1919, 687A.
[43] *J.*, 1919, 49R.
[44] *Chem. Umschau*, 1919, **26**, 89 ; *J.*, 1919, 645A.
[45] *J.*, 1918, 430A.

and it seems likely that the oil will have a definite Reichert-Meissl value.

The discovery of an interesting new oil palm, *Elæis poissonnii*, is reported from the Cameroons.[46] The fruit of this palm yields products similar in nature to the ordinary African palm, *Elæis quineensis* (Jacq.). Two varieties of the palm have been identified and their fruits are contrasted below with the fruit of the Lisombe palm.

	Tenera %	Dura %	Lisombe %
Pericarp	76	44	61·5
Nuts	21	56	38·5
Yield of oil from pericarp . .	70·25	58·6	63·15
„ „ the whole fruit	53·50	55·8 ?	38·35

Owing no doubt to the result of control, our ideas of the relative values of oils and fats have had to be revised. In this country we have seen cacao butter being sold as a culinary fat, and in this connection may be noted a patent [47] for deodorising cacao butter by means of steam at a high temperature in the presence of water-bearing starchy matter such as chopped raw potatoes.

R. H. Ellis and E. M. Hall [48] show from a large number of analyses that the published range of iodine values for palm kernel oil are too low and give as their limit in values 16 and 23. Their view that the discrepancy is due to the older figures having been obtained by means of Hübl's solution, which they assume to give lower values than are obtained by means of the Wijs solution, is, however, untenable. A large number of the figures quoted by Lewkowitsch were actually obtained by means of the Wijs solution and a number examined by the present writer 15 or 16 years ago gave figures varying between 14 and 16. The explanation must rather be looked for in the change in character of the oil, possibly due to the nuts being collected over a wider area. The iodine value of coconut oil shows the same upward tendency, although in a less degree.

In an instructive report on the crude cohune nut [49] it is stated that one district in Honduras is capable of yielding 10,000 tons per month. The oil belongs to the coconut oil group, and the methods used for refining and deodorising coconut oil should be applicable, when cohune oil would be suitable for margarine making. The nut has a hard, thick shell from which when carbonised an extremely absorbent charcoal can be obtained simulating in this respect coconut shell.

[46] Fauchère, *Bull. Off. Colon*, 1918, 11, 86; *J.*, 1918, 741A.

[47] Co-operative Wholesale Soc., G. Martin, and W. H. Brizell, Eng. Pat. 122512; *J.*, 1919, 196A.

[48] *J.*, 1919, 128T.   [49] *U.S. Comm. Rept.*, June, 1919; *J.*, 1919, 312R.

WAXES.

The wax obtained from shuei flowers (*Jasminum odoratissimum*) has been examined by R. Tsuchihashi and S. Tasaki,[50] who found the following figures: Sp. gr. at 100° 15° C. 0·8259, m.pt. 45°·47° C., n_D^{60} 1·4622, $(a)_D^{15}$ 0·11, acid value 1·25, saponification value 100, Reichert-Meissl value 1·0. The unsaponifiable matter is stated to consist mainly of triacontane, $C_{30}H_{62}$, but this must be accepted with reserve as the difference between the acid value and the saponification value points to the presence of a fair amount of an alcohol

J. Gadamer [51] has examined a wax from the Brazilian wild bee of the *Melipona* or *Trigona* species. The following figures are given: m.pt. 66° C., sp. gr. 0·9898, acid value 26·5, ester value 57·3 59·2, ratio number 2·23. There is also given a statement of the composition of the wax which must be accepted with reserve

On extracting the pressed residues from beeswax with petroleum spirit of low boiling point, G. Buchner [52] obtained a wax having an acid value of 21·24, an ester value of 59·82, and a ratio number of 2·8. On using for the extraction petroleum spirit of higher boiling point, chloroform, and carbon tetrachloride, waxes were obtained having acid values lying between 20·3 and 23·45, saponification values between 85·43 and 94·39, and ratio numbers between 3·0 and 3·2. A sample of African beeswax had the following characteristics: Sp. gr. at 15° C. 0·96, m.pt. 61°·65·4 C., iodine value 11·65, acid value 19·92, ester value 79·45, ratio number 3·98

The following figures are given for candelilla wax as representing the average results obtained: Acid value 16·96, ester value 33·86, hydrocarbons 52·52%.

GLYCEROL.

The work of outstanding importance is the development of the process of manufacturing glycerin by the fermentation of sugar by means of a yeast. J. R. Eoff, W. V. Linder, and G. F. Beyer [53] obtained the best results with a variety of *S. ellipsoideus* and found a yield of between 20 and 25% of glycerol from molasses, a considerable amount of alcohol being formed as a by-product. It is stated that the yeast must be bred by successive sowings and must be inured to the presence of sodium carbonate. These authors find that the gradual addition of soda ash is the best method of accelerating the reaction. The presence of ammonium chloride is also stated to be beneficial. Their communication is ably summarised from a fermentation point of view by A. R.

[50] *J. Chem. Ind. Tokyo*, 1918, 21, 1117; *J.*, 1919, 117A.
[51] *Arch. Pharm.*, 1917, 255, 425; *J.*, 1919, 730A.
[52] *Chem.-Zeit.*, 1918, 42, 373; *J.*, 1919, 871A.
[53] *J. Ind. Eng. Chem.*, 1919, 11, 842; *J.*, 1919, 780A.

Ling.[54]   The process has been patented in the United States by J. R. Eoff.[55]

A similar process has been elaborated in Germany by W. Connstein and K. Ludecke,[56] who add sodium sulphite as an accelerator in place of sodium carbonate, obtaining thereby practically the same yield of glycerol as is obtained in the American method.

The use of sodium sulphite has also been proposed by K. Schweitzer,[57] who states that an increase of 1·3% of glycerol can be obtained. The production of glycerin in Germany by the fermentation of sugars is stated to have amounted to 1000 tons per month.

J. W. Yates [58] introduces the use of sodium aluminate as a coagulating agent for the impurities in glycerin lyes obtained from waste fat His results show that by the use of this reagent he was able to reduce the amount of organic impurities in 80% glycerin from between 7 and 9% to 2·1%. He gives some analyses showing that this treatment is more efficacious than treatment with aluminium sulphate. Possibly this method will be useful in the treatment of glycerin obtained from rank fish oils which are sometimes " fiery " during nitration.

A method claiming to attain the same object [59] consists in heating the glycerin lye with a caustic alkali or alkaline-earth to between 100° and 120° C., whereby the impurities are said to be decomposed. There is a danger, however, of causing the formation of polyglycerols.

H. Wolff [60] has published some figures for the specific gravities and refractive indices of two glycerin solutions, which are in fairly close agreement with those given by Gerlach. The temperature correction to be applied to the refractive index for a solution containing 86% of glycerol is $2·8 \times 10^{-4}$, and for a solution containing 76·72% $2·6 \times 10^{-4}$ for each degree Centigrade. These figures are useful as the determination of the refractive index affords a ready means of checking the percentage of glycerol in pure solutions.

P. Bertolo [61] deprecates the use of barium carbonate as a means of neutralising the acid glycerin liquors obtained in the Twitchell process of hydrolysis owing to the alleged difficulty of removing the excess of barium. He prefers to neutralise first with a slight excess of lime, the precipitate from which after cooling is filtered off and the clear liquor evaporated to sp. gr. 1·116. This liquor is then boiled and treated with a slight excess of barium hydroxide After again cooling and filtering, the excess of barium is removed with cautious addition of oxalic acid. This, in the writer's opinion, is a wholly unnecessary procedure.

54 J., 1919, 175R.   55 U S. Pat. 1288398 ; J , 1919, 194A.
56 Ber., 1919, 52, 1385 ; J , 1919, 691A
57 Schweiz. Chem. Zeit., 1919. 18 ; J., 1919, 230R.   58 J., 1919, 94T.
59 Billwärder Seifen- u. Glycerinfabr., Ger Pat. 310606 , J., 1919, 913A.
60 Z. angew. Chem., 1919. 32. 148 ; J . 1919, 470A.
61 Annali Chim. Appl., 1919, 12, 24 ; J., 1919, 832A.

HARDENED FATS.

This industry has expanded to great dimensions, but unfortunately no statistics are available for this country. Even in Russia,[62] where the process is only in its infancy, the production of hardened fats reached the total of 1600-1900 tons per month in 1918, principally from sunflower oil.

There have been a considerable number of patents taken out in connection with this industry, chiefly, however, for minor improvements in plant or additions to existing patents.

Among the new uses to which hardened fats have been put may be noted that suggested in a patent by C. Ellis,[63] who introduces it as an ingredient for phonograph records.

S. Ueno [64] has investigated the effect of a large number of substances upon the rate of the hydrogenation of oils. Some rather surprising results are recorded. Thus, the soaps of magnesium and barium are stated to act as retarding agents, whereas the soaps of calcium, strontium, and aluminium had no action. Boric acid also is stated to have an inhibiting effect which is surprising in view of the fact that nickel borate has been repeatedly proposed as a catalyst.

The same observer [65] also expresses the velocity of the absorption of hydrogen by oils by the equation

$$k = \frac{1}{t} \log_n \frac{a}{a - x}.$$

C. W. Moore [66] contributes a long and interesting paper on the formation of "iso-oleic acid" during the hydrogenation of oleic acid. From the results of his investigation he concludes that "iso-oleic acid" is a mixture of elaidic acid, which contains the double bond in the same position as ordinary oleic acid, and one or more acids in which the double bond has migrated further away from the carboxyl group. A statement made by the author that the formation of "iso-oleic acid" only takes place concurrently with hydrogenation is at variance with the experience of the writer, as in the experiments made by Lewkowitsch quoted by the author wherein large amounts of "iso-oleic acid" had been formed when using a copper catalyst, no reduction of iodine value has taken place.

The first results of a research of great theoretical interest have been communicated by E. F. Armstrong and T. P. Hilditch [67] on the rate of absorption of hydrogen by unsaturated fatty oils. From their curves

[62] *J.*, 1918, 476R.
[63] U.S. Pats. 1276507 1276509; *J.*, 1918, 774A.
[64] *J. Chem. Ind. Tokyo*, 1918, 21, 898; *J.*, 1919, 20A.
[65] *J. Chem. Ind. Tokyo*, 1918, 21, 749; *J.*, 1919, 21A.
[66] *J.*, 1919, 320T.
[67] *Proc. Roy. Soc.*, 1919, A, 96, 137; *J.*, 1919, 780A.

it appears that the more highly unsaturated glycerides are first hydrogenated. They call attention to points of similarity between this reaction and that taking place when glucosides are hydrolysed by means of enzymes, and deduce the existence of an unstable substance of complex structure containing nickel and the unsaturated compound.

L. Ubbelohde and T. Svanoe [68] have contrasted the process of hydrogenation using cottonseed oil and whale oil in apparatus simulating on a laboratory scale the commercial plants of Normann and Wilbuschewitsch and Erdmann. They state that the rate of absorption of hydrogen increases up to 170° C., and then very slightly up to 200° C., no increase in the rate taking place above that temperature. This is contrary to the present writer's experience, who has found on a laboratory scale a material increase in the rate of absorption up to 240° C.

In the type of machine used by Normann and Wilbuschewitsch there was a perceptible increase in the rate of absorption obtained by increasing the amount of catalyst up to a maximum of 2·4%. It was further found that by increasing the agitation and also the pressure up to certain limits the time could be shortened. In confirmation of the work of C. W. Moore (see above), it was noticed in the case of cottonseed oil the iodine value of which had been reduced by hydrogenation to about 90, that there was a great difficulty in separating the unsaturated fatty acids by the lead-salt-ether method due to the presence of a solid unsaturated fatty acid having a lead salt difficultly soluble in ether. This is ascribed by the authors to the formation of a solid isomeride of oleic acid by the partial reduction of the linolic acids. It is also possible the oleic acid itself has been changed into a solid modification.

G. Riess points out [69] the danger of loss of nickel incurred during the incineration of the fat in preparing the ash and advocates the extraction of 200 grms. of fat with 100 c.c. of 12·5% hydrochloric acid containing a few crystals of potassium chlorate. He then proceeds with the dimethylglyoxime test in the usual way. By this method a commercial sample of hardened arachis oil which appeared free from nickel when tested in the ordinary manner was found to contain 1·8 mgrms. of nickel per kilo. The same observer found arsenic up to 0·456 mgrm. per kilo. by Beck and Merres' modification of Smith's colorimetric test, although a modified Marsh's test gave negative results.

If it is certain that arsenic was really present it has probably been introduced through impure hydrogen which had most likely been caused by conditions engendered by the war.

F. F. Nord [70] has studied the conditions favouring the hydrogenation of oils using palladium chloride as a catalyst. In view of the high

[68] Z. angew. Chem., 1919, 32, 257, 269, 276; J., 1919, 870A.
[69] Arb. Reichsgesundheitsamte, 1919, 51, 521; J., 1919, 913A.
[70] Z. angew. Chem., 1919, 32, 305; J., 1919, 913A

cost of palladium this method is not likely to supersede the common one employing nickel. The only possible advantage it offers is that hydrogenation takes place at a much lower temperature. The author states that when castor oil is hydrogenated by this method the hydroxyl groups are split up, whereas in the present writer's experience, using nickel as a catalyst, a temperature of 200° C. is necessary before the hydroxyl group is affected
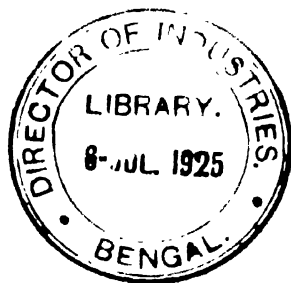
PAINTS, PIGMENTS, VARNISHES, AND RESINS.

By J. H. B. Jenkins,

Chief Chemist, Great Eastern Railway Co.

In the progress of such an art as painting, a special value must always attach to big-scale experiments when conducted under the responsible supervision of a scientist, and the results now available [1] of further extensive field tests by J. N. Friend as to the exposure properties of different paints, and the best conditions of application, deserve careful consideration. The paints were generally applied to metal plates, which were then exposed to ordinary weathering for periods up to $2\frac{1}{2}$ years.

Amongst the questions investigated was the advisability of removing completely the original oxide from the surface of the mild steel plates before painting them. Some of the plates were left in the " black," whilst others were freed from all oxide or scale either by sand blasting or, in other cases, by acid pickling. The paint was then applied, and the effects of long exposure studied. In the issue Friend speaks very definitely : that it is the best practice " to paint structures while their scale is still on, after of course removing any loosely adherent flakes and rust." Indeed he goes further and extends this opinion to ordinary rusting. Provided that any hard lumps are removed he regards the rust itself as a desirable pigment, awaiting only the oil to convert it into a paint. The complete removal of rust by sand-papering he regards as a mistake.

In previous work Friend has shown that in the drying of linseed oil, so long as the main chemical change is one of oxidation, the skin expands with attendant crinkling, but in later changes volatile products are given off in larger quantities, with resultant contraction and cracking of the old paint surface.

The opinion of Liebreich and Spitzer that one thick coat of paint is more protective than several thinner coats seems doubtful, and Friend draws the opposite conclusion, finding the advantage to lie with the thinner coats, provided the same aggregate thickness is attained.

[1] *Carnegie Schol. Mem., Iron and Steel Inst.*, 1918, **9**, 77 ; *J.*, 1918, 736A.

Special interest attaches to experiments made to see if the colour of the pigment is a factor in determining the life of a paint. Wooden panels and iron plates were used, and to serve as pigments, lakes of similar character but different colours were applied as paints The conclusion arrived at is comprehensive : so long as air is excluded, light does not make linseed oil set, nevertheless light does promote the rate of setting or drying in the presence of air ; the acceleration depends upon the colour, the short light waves being the most active. This prepares us for the results of the experiments, which have already been implied by the North Dakota tests for 1906 When white or bluish paints are used, the accelerated chemical action on exposure leads to the early disintegration of the paint surface, and for preserving effect red or dark paints are to be recommended for surfaces exposed to daylight

In view of the distinction now being drawn between oxidation and polymerisation changes in linseed oil during thickening or setting, Friend finds that when raw linseed oil is used as a coat, so that the drying changes are due to oxidation, the resultant linoxyn is permeable to moisture. This porosity makes raw linseed oil a less effective preservative than polymerised linseed oil, that is to say than such oil as, prior to its application, has been heated to a sufficiently high temperature to be thickened by polymerisation Substantially this implies that " boiled " oil forms a better preservative coating than raw oil.

PROPERTIES OF DRYING OILS.

In the ordinary process of boiling linseed oil both oxidation and polymerisation occur To study the two changes separately is mainly the object of some work by H. Ingle and A. Woodmansey.[2] Boiled oil, in which the changes have been effected at about 260 C, is taken as the type of a predominantly polymerised oil, whilst blown oil prepared by blowing air through the oil at 60 100 C is adopted to represent oxidised oil. Both processes produce more or less insoluble portions which, however, differ chemically. The authors retain the term linoxyn to refer to ether-insoluble portions from blown oil, and suggest the names polyolin and poly-acids respectively for the ether-insoluble fractions obtained from highly polymerised linseed oil and the corresponding ether-insoluble acids Polyolin is shown to be a remarkably stable and elastic substance. A newly made sample had an iodine value of 53, it yielded on hydrolysis 90% of fatty acids, just half of which was insoluble in petroleum spirit, this portion having a combining weight of 384·4. The polyolin was found to contain 4·7% of ash, the nature or source of which is not stated, and only 5·3% of glycerol, etc.

[2] J., 1919, 101т.

The authors think that in the condensation the position of the double linkages in the molecules is not fixed, and that when the linolic and linolenic acid radicles polymerise, ring formations result with a structure suggestive of rubber such as

$$--\text{CH}-\text{CH}\quad\text{CH}\quad\text{CH}$$
$$-\text{CH}\quad-\text{CH}\quad\text{CH}\quad-\text{CH}--$$
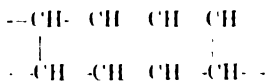
offering considerable resistance to oxidation, though the products still possess a considerable iodine value.

From polymerisation the authors turn to oxidation changes, and give the analytical results of the examination of linseed oil in different stages of oxidation, and a suggestion is made of a course of changes as follows : Assuming a mixed glyceride with linolenic, linolic, and stearic acid radicles, the initial change is an oxidation of the first two of these radicles with the formation of peroxides. At this stage the glyceride exhibits neither the insolubility of oxidised fatty acids, nor the solubility of the unoxidised (stearic) acid ; the glyceride has become intermediate in solubility, being soluble in methylated ether but insoluble in petroleum spirit. In the subsequent period, that of "ageing," further oxidation is not represented, but the mixed glyceride in its already oxidised condition, suffers a molecular rearrangement in which 3 molecules of mixed glyceride become 3 molecules of simple glycerides, of glyceryl tri-stearate, of glyceryl tri-oxylinolate, and glyceryl tri-oxylinolenate, the latter two forming the final insoluble " linoxyn " of oxidised oil.

The authors have made a partial investigation of " superoxidised oil," the term being applied to the sticky and viscid mass to which linseed oil degenerates long after its solidification by drying is complete. The development of free acidity is a characteristic, and the authors suggest that this may be due to spontaneous decomposition of peroxides by which the chain is broken at parts with the formation of aldehydes, which by subsequent oxidation give rise to acids, etc. Thus,

$$a.\qquad \begin{array}{c}-\text{CH}-\text{CH}--\\ |\quad\quad|\\ -\text{O}\quad\text{O}\end{array}\quad -2\ \begin{array}{c}-\text{CH}\text{l}\\ \|\\ \text{O}\end{array}\quad \xrightarrow{+\text{O}}\ 2\ \begin{array}{c}--\text{CO}\\ |\\ \text{OH}\end{array}$$
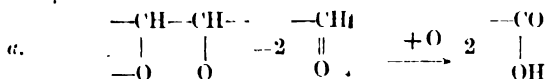
Or by reaction of the peroxides with water.

$$b.\qquad \begin{array}{c}--\text{CH}-\text{CH}--\\ |\quad\quad|\\ \text{O}\quad\text{O}\end{array}\ +\text{H}_2\text{O}\ \begin{array}{c}-\text{CH}_2\\ |\\ \text{OH}\end{array}\ +\ \begin{array}{c}-\text{CO}\\ |\\ \text{OH}\end{array}$$
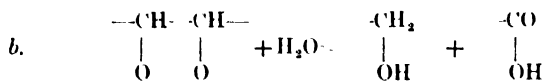
The authors conclude (cf. Friend, ante) that " for permanency, a polymerised oil (boiled oil) is superior to an oxidised oil as a paint vehicle."

Incidental to their work is the examination of the mucilaginous matter, the so-called "frog spawn" or "break" coagulated and precipitated during the boiling of linseed oil This substance is stated to suffer oxidation preferentially to the oil, and is probably a form of lecithin which decomposes at high temperatures with the liberation of trimethylamine The fishy smell of this sometimes leads to mucilaginous linseed oil being suspected of adulteration with fish oil.

Manganese driers are found to be far more active than lead driers, but their use in place of lead driers leads to less permanent products.

E J Sheppard [3] has studied the effect of exposure to air of raw linseed oil, and finds that with oil in layers 1 cm thick a skin forms when the increase in weight is about 6%. The decrease of iodine value seems to have a straight line relationship to the increase of specific gravity The development of free acidity, however is more irregular.

H. A. Gardner [4] has noted the changes on keeping about 30 different paint oils in pint bottles with about 1 inch air space, the bottles being kept closed and exposed to indirect sunlight The changes were noted after each 3-year period When a considerable amount of material had separated the latter was found to be highly acid Fish oils and marine animal oils were specially liable to develop free fatty acids Perfect clarity and freedom from moisture help much in the keeping qualities, and the same improvement seems to follow sterilisation by heating to 105°C The changes which attend exposure are ascribed largely to aero-hydrolysis due to the presence of either moisture or fat-splitting enzymes In the course of years tung oil was found to have changed mostly to a white solid mass

An investigation of the cause of the more rapid "setting" of paint and varnish during moist weather has also been made by H A Gardner [5] Films exposed respectively to dry and moist air were compared. In moist air the gain in weight in 24 hours was almost equal to the gain in dry air in 48 hours. But this initial gain was in both cases followed by an almost equal loss, which, however, in moist air was followed by a fresh increase and loss The first gain and loss is taken to be due to oxidation at the double bond positions, followed by formation of decomposition products of oxygenated compounds In the film exposed to moist air the second increase corresponds to the hydrolysis of the glyceride, forming glycerol and fatty acids, followed by decomposition with formation of formic acid, etc The final hardness was greater in the film exposed to dry air.

The same author [6] discusses the conditions of use of menhaden oil

[3] J. Ind. Eng. Chem , 1919, 11, 637 ; J., 1919, 588A.
[4] J. Ind. Eng. Chem., 1919, 11, 759 ; J., 1919, 912A.
[5] Circ. 70, Paint Manuf. Assoc. U.S., Aug., 1919 ; J., 1919, 832A.
[6] Circ. 68, Paint Manuf. Assoc. U.S.; J., 1919, 833A.

and kindred oils in paints and varnishes   He also shows [7] that under favourable conditions and treatment soya oil may be made to dry almost as rapidly as boiled linseed oil.   A drier containing 0.03% manganese, 0.20% lead, and 0.01% cobalt is recommended, the metals being present as " linoleates."   Heat treatment followed by blowing is advisable.

Perilla oil,[8] obtained from the seed of the Asiatic mint (*Perilla ocymoides*), is made in considerable quantities in Japan, and is used there largely as a drying oil in substitution for linseed oil.

Safflower oil as a drying oil has been studied by H H Mann and N. V. Kanitkar.[9]   *Roghan* or " Atidi wax ' is produced by boiling the oil for two hours, and then putting it into vessels partly filled with water.   The authors think that the solidified product is the result of decomposition followed by polymerisation, oxidation only playing a secondary part.   Some anomalies are met in the use of safflower oil as a drying oil ; but when it is heated with white lead, without further driers, a far more glossy surface is left than when boiled linseed oil is used.

L. H. Baekeland [10] has patented a method of preparing tung oil for coating articles   The oil is heated to a temperature just short of that producing solidification, then heated to a lower temperature in contact with the article to be impregnated " which causes solidification of the oil."   The article thus treated is coated externally by an infusible and insoluble phenolic condensation product.   A modified tung oil is prepared stable up to 100° C and solidifying about 160 C.

LINSEED OIL FATTY ACIDS

The imperative demand for glycerin during the war, coinciding with a general shortage of fatty oils, resulted in the fatty acids from linseed oil being tried as a substitute for the glyceride in paint and varnish making.   Several questions arose : Would the fatty acids, now free to function separately, have an effect differing obviously from their action when represented in the mixed glyceride ?   And if so, would such difference be mainly evident in their susceptibility to atmospheric conditions, to reaction with the pigments, or to action on the surface to which they were applied   for example, when they were used in a dressing for waterproof sheeting, would the fatty acids lead to a " tendering " of the sheet fabric ?   It is probable that the full potentialities of the fatty acids as a paint medium were not realised during the limited period of emergency, nevertheless the experience obtained in the use of so abnormal a paint medium should be on record.

[7] *Circ.* 69, *Paint Manuf. Assoc. U.S.*; *J.*, 1919, 833A.
[8] *J.*, 1919, 45R.   [9] *J.*, 1919, 36T.
[10] U.S Pat. 1312093 ; *J.*, 1919, 730A.

The following opinion of R S Morrell [11] may be taken as representative. As a preliminary step he finds it advisable to separate from the commercial fatty acids the solid constituents in suspension which consist mainly of the more saturated acids. The liquid portion can be thickened without loss by special methods so as to yield a lithographic oil of low grade which in emergency might find application in printing inks. For drying liquors and binding sizes favourable results have been obtained. When used in conjunction with certain pigments of an inert character paints were obtained giving fair results, but generally the quality of the material is much inferior to that of linseed oil, and the durability is poor. Fairly satisfactory stoving and stamping varnishes, and also japans and black enamels, can be prepared from it. An initial objection to the use of such fatty acids for ordinary varnish making is the extent to which they darken on being heated, and to this has to be added a marked want of durability when the varnish films are exposed to free weathering conditions, the resistance to water being very slight For indoor work, however, this objection has less force ; the resulting coats have good lustre, but are rather brittle. Generally the defect is seen in inferiority both in elasticity and body.

L. Archbutt's experiments [12] lead him to substantially the same conclusions. He finds a pronounced inferiority when the fatty acids are used in paints for outside surfaces iron plates so painted showing deterioration of surface shortly after exposure to the weather The following observations by him on the interaction of iron and linseed oil fatty acids in the production of a drying oil are of interest. In the absence of moisture there is no sensible reaction, but in the presence of water, when iron turnings and the fatty acids are brought into contact, a considerable proportion of iron passes into solution, with evolution of gas. The resultant liquid when exposed to air darkens rapidly to a brown colour, and finally to a rich, red-brown colour.   It is only when it has attained the latter colour that the liquid has the property of drying like an ordinary boiled oil Three or four per cent. represents the approximate amount of iron necessary to ensure good drying, provided that not less than about 70% of the iron present is in the ferric condition. Such a paint medium is not suitable, owing to its colour, for use in making up white or very light coloured paints, but oxide of iron, umbers, ochres, blacks, and other inert pigments are suitable Pigments such as white lead, zinc white, and colours which are chemically reactive with the fatty acids cannot be used. The gloss and general appearance of the resultant coats, both on metal and wood, are quite satisfactory, but as judged after a year's exposure under outdoor conditions, single coats are decidedly permeable, and do not compare well with linseed oil paints.   Two coats give, however, a fair amount of protection, though still not so good as linseed oil paint.

[11] Private communication.   [12] Private communication.

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The experience in the use of linseed oil fatty acids instead of the glyceride for dressing waterproof sheets (tarpaulins) was also such as to lead to a reversion to normal dressing as soon as the latter became available The sheets dressed with the treated linseed oil fatty acids dried somewhat hard and stiff; there was nevertheless evidence of the successive coatings not having an even hold on each other, and further a tackiness soon developed giving much trouble when the sheets were folded The lines of the folds, too, showed cracks. The chances of getting a good waterproof sheet seemed greater when cotton sheets, instead of flax sheets, were dressed, probably owing to the greater quantity of dressing taken up by the cotton sheets Generally, however, the sheets proved less impervious to water than sheets prepared with normal linseed oil dressing

Broadly the sheets proved wanting in flexibility and durability. There is no clear evidence as to " tendering " of the fibres- -anyway it was not a prominent feature in the period during which these sheets were under observation

Amongst the patents taken out for the treatment of linseed oil fatty acids so as to obtain a satisfactory paint medium may be mentioned one, by O. Wilkins and Co. and W. M. Allsebrook,[13] in which the reactions between the fatty acids and metals such as iron are covered ; by A. A. Lockwood and M. R. Samuel,[14] where a borate is formed, followed by oxidation ; by A P. Bevan,[15] who separates the stearic acid by limited treatment with e q. calcium hydroxide, and then adds cobalt resinate as a drier.   E. C. Witter [16] heats the fatty acids to 500°–600° F. for 4 hours, with or without driers, with further treatment if the product is required for linoleum manufacture, and F. Boehm and C. A. Reihl [17] heat to a high temperature in the presence of a small proportion of metallic copper, nickel, or cobalt, and blow in oxygen till a sp. gr. of 0·992–0·998 is attained.   It is an advantage to add 12 15% of tung oil and, a small quantity of alkaline-earth soap to increase speed of polymerisation

PIGMENTS.

The qualities of white lead have evidently to be kept in mind as a standard in considering the following special properties claimed by W. H. Hendricks [18] on behalf of zinc oxide as a pigment : whiteness, permanence, fineness of division, oil absorption, inertness towards other pigments, durability, and non-toxicity ; the resultant paint film is markedly glossy and smooth ; exposure does not make it crumble or " chalk," and it remains opaque. As qualifying these properties it is observed that owing to the extreme fineness of the particles of

[13] Eng. Pat. 122015 ; *J.*, 1919, 111A.   [14] Eng. Pat. 121237 ; *J.*, 1919, 110A.
[15] Eng. Pat. 121992 ; *J.*, 1919, 110A.   [16] Eng. Pat. 122696 ; *J.*, 1919, 187A.
[17] Eng. Pat. 123792 ; *J.*, 1919, 263A.   [18] *Chem. Trade J.*, 1919, **65**, 603.

zinc oxide, when it is used as a single pigment in a paint it spreads out excessively under the brush, so that the resultant coat is so thin as to appear somewhat transparent The difficulty in fact is to get single coats of zinc oxide paint of sufficient thickness to compare satisfactorily with, say, a white lead paint, which forms both a much thicker coat, and one with a rougher surface This rougher surface of a white lead paint is not altogether a disadvantage, it offers a good " bite " for later coats, though it unfortunately offers a corresponding hold for dirt, and cannot be kept so clean by washing. The different modes of deterioration of the two paints are also significant. Zinc oxide paints do not progressively crumble and " chalk," but peel off finally in patches.

The white lead paint film not only crumbles progressively and " chalks," but cracks appear in the film, at first of microscopic dimensions, forming a fine network pattern all over the surface (" checking "). These cracks enlarge and become selective lines of attack for the action of sun and rain. White lead and zinc oxide are in these properties largely complementary to one another, and in judicious admixture they produce a more perfect paint than either constituent when used alone. A general statement is made to the effect that a single-pigment paint, whatever the nature of the pigment, is never so satisfactory as one made up with a combination of pigments.

The development of white pigments and inert fillers or " extenders," especially in respect to American practice, is also dealt with in a paper by S. J Cook.[19] The methods of manufacture of the pigments are described, the resultant products being dealt with according to whether they are the results of wet precipitation, such as white lead and lithopone, or are fume products, like basic lead sulphate, zinc oxide, and " leaded-zinc." The latter is derived from zinc ores containing large quantities of lead, and the resultant product is graded according to its content of basic lead sulphate up to say 35%.

White lead paint dries to a rather soft surface, weathering to a chalky coat, easily abraded. White zinc (zinc oxide) paint dries more slowly, but yields a hard, almost vitreous surface. A mixture of the two such as 60% white lead and 40% zinc oxide shows a material correction of qualities, and is recommended. As to the inert fillers or " extenders," they are not invariably to be regarded as diluents, and remarks are made from this point of view on barytes and blanc fixe, also precipitated barium carbonate, silica, gypsum, kaolin, and asbestine.

Lead Pigments.

Some useful observations on the oxides, carbonates, and sulphates of lead were made by C. A Klein[20] in a paper read before the Oil and Colour Chemists' Association. " New process " lead oxide, obtained

[19] J., 1919, 137T.   [20] J., 1919, 471A.

by violent agitation of molten lead in cast-iron containers in a current of air, is brown to yellow in colour, and may contain 4–7% metallic lead. Sublimed oxide, an American product, is obtained by oxidising lead and subliming the resultant oxide, using natural gas as a source of heat. Orange lead differs from red lead in its higher content of PbO_2, the theoretical proportion of 34·94%, however, never being attained. It is suggested that Pb_3O_4 possibly consists of a solid solution of PbO and PbO_2. There are also observations on the successive changes in white lead during its formation from the basic acetate. Basic lead sulphate, obtained by sublimation of galena, has found extensive application as a constituent of paints in the United States.

Luminous Paints.

Bahr [21] discusses the phenomena of luminescence in relation to luminous paints from certain theoretical considerations. The photo-luminescence of alkaline-earth sulphides results from the crystalline structures and the presence of small quantities of such impurities as bismuth, lead, or copper. With increase of atomic weight and of di-electric constant, the radiation emitted moves towards the spectrum zones of longer wave lengths. Self-luminous paints are produced by admixture of radio-active matter with zinc blende, a good binding material being a pure nitrocellulose lacquer. A patent for luminous paint was taken out by G. A. H. Muller and J. Macfarlane, [22] who heat sulphur (26 parts) with strontium sulphate (19), calcium sulphate (6), and magnesium carbonate (1 part), the product being then ground.

Carbon Blacks.

Amongst the patents for methods of preparing carbon blacks some novelty appears in that taken out by C. D. McCourt and C. Ellis, [23] who force methane through strongly heated porous material, using the liberated hydrogen as fuel and collecting the gas black. T. W. S. Hutchins [24] allows the electric arc to impinge on a vertically rotating disc which brings up a film of oil or tar from the bath, but in a subsequent patent [25] he substitutes an oxy-hydrogen or similar high-temperature flame for the arc. To render lamp-black dustless E. L. Curbishley [26] incorporates with it 2-5% of resin oil. L. Bendit [27] precipitates the carbon in a zone of reduced pressure by electrostatic action.

[21] J. Gasbeleucht., 1918, 61, 604, 614 ; J., 1919, 110A.
[22] Eng. Pat. 130885 ; J., 1919, 730A.
[23] U.S. Pat. 1276385 ; J., 1918, 708A.
[24] Eng. Pat. 124557 ; J., 1919, 378A.
[25] Eng. Pat. 126560 ; J., 1919, 472A.
[26] Eng. Pat. 127770 ; J., 1919, 545A.
[27] U.S. Pat. 1304729 ; J., 1919, 590A.

SYNTHETIC RESINS.

Coumarone Resins.

Attempts continue to be made to produce fully satisfactory paint-resins by polymerising indene and coumarone, two prominent constituents of the fraction of coal tar naphtha distilling between 160° and 185° C. The early claims made on behalf of the resultant resins for special resistance to alkalis and acids have not escaped challenge, but the properties are influenced greatly by the methods adopted to induce polymerisation, and in this we have a field for progressive investigation. Means have been described for distinguishing these from other resins, natural and synthesised. Thus, J. Marcusson [28] points out that the natural resins melt at higher temperatures, and have much higher acid, saponification, and iodine values; further, they are optically active. The greater solubility of coumarone resins in solvents is also noticed. H. Wolff [29] deals with the means of separating the coumarone resins from oxidised fatty acids.

M. Darrin [30] produces a light-coloured coumarone resin by the action of sulphuric acid on the indene-coumarone constituents, followed by neutralisation and distillation. F. W. Sperr and M. Darrin [31] heat the naphtha fraction under high pressures to temperatures of 100° 150° C., and, to assist in the polymerisation, use as catalysts strips of copper, silver, gold, or platinum. The Koppers Co. [32] also produce polymerisation by heating the coumarone-containing liquid under pressure in an autoclave. According to another patent. F. W. Sperr and M. Darrin [33] produce a paint by dissolving pitch in the selected fraction of naphtha, which is polymerised by the use of such a catalyst as aluminium chloride, or by steam or air at 160° C

E. Stern [34] gives the results of an examination of coumarone and finds that the polymerisation is reversible. He finds that zinc chloride and silicon tetrachloride do not induce condensation, but that tin tetrachloride has a pronounced effect. The action of aluminium chloride is not due to the liberation of hydrochloric acid. Coumarone oils, though not oxidisable themselves, yet leave dry films under the influence of paint " driers " acting as catalysts. The properties of mixtures of coumarone oils with boiled and raw linseed oil are noticed.

[28] *Chem.-Zeit.*, 1919, **43**, 109, 122 ; *J.* 1919, 329A
[29] *Farben Zeit.*, 1918, **23**, 307 ; *J.*, 1919, 646A.
[30] U.S. Pat. 1297328 ; *J.*, 1919, 428A.
[31] Eng. Pat. 123806 ; *J.*, 1919, 263A
[32] U.S. Pat. 1296776 ; *J.*, 1919, 379A.
[33] Eng. Pat. 118079 ; *J.*, 1919, 46A.
[34] *Z. angew. Chem.*, 1919, **32**, 246 ; *J.*, 1919, 688A.

Bakelite type of Resins.

Activity is still obvious in the preparation of phenol-aldehyde condensation products. T. A. Edison [35] adds p-phenylenediamine to the usual constituents. R. E. Dior,[36] to assist in the condensation, employs as catalysts such substances as the ammonium salt of a volatile organic acid or ammonium bicarbonate, for example, 3 gallons of 40% formaldehyde, 5·5 gallons of commercial carbolic acid, and 6 lb. of ammonium bicarbonate. H. V. Potter and the Damard Lacquer Co.[37] somewhat similarly use a small quantity of alkali such as ammonia as a catalyst. L. H. Baekeland [38] produces a fusible product of the saliretan class by condensation of a cresol mixture containing p-cresol with a compound containing a mobile methylene group. E. Beckmann and E. Dehn [39] use furfural in place of formaldehyde in the preparation of these. E. Zimmermann [40] produces a resinous substance by condensing formaldehyde with lactic acid heated to 100°-200° C.

NATURAL GUMS AND RESINS.

The Board of Trade Journal [41] describes the methods adopted for separating Kauri gum from extraneous matter, and includes some statistics of the gum industry in New Zealand. W. Fahrion [42] publishes the properties of the soda-soluble constituents of pine resin, including their solubility after acidification. W. Schaefer [43] deals with the recovery of rosin from pine scrapings. A. Zinke [44] working with H. Lieb has studied siaresinol and other derivatives from Siamese gum benzoin, and with E. Unterkreuter [45] has investigated the hydrocarbon constituents of β-dammar resin. H. Wolff [46] finds that borax solutions do not effect any sharp separation of one resin from another, but only a concentration of one or other; for example, although colophony when alone is not dissolved, yet it is partly soluble in borax solutions when in admixture with shellac. W. Fahrion [47] discusses the comparative chemical properties of Austrian and American rosins. E. Knecht and E. Hibbert [48] conclude from their investigations

[35] U.S. Pat. 1283706; J., 1919, 47A.
[36] Eng. Pat. 124010; J., 1919, 330A.
[37] Eng. Pat. 131112; J., 1919, 834A.
[38] U.S. Pat. 1306681; J., 1919, 590A.
[39] Sitzungsber. K. Preuss. Akad. Wiss., 1918, 1201; J., 1919, 646A.
[40] Ger. Pat. 305775; J., 1919, 187A.
[41] Bd. of Trade J., Nov. 28, 1918, and May 22, 1919; J., 1918, 456R; 1919, 207R.
[42] Chem. Umschau, 1918, 25, 3; J., 1918, 774A.
[43] Chem. Umschau, 1918, 25, 25; J., 1918, 775A
[44] Monatsh Chem., 1918, 39, 627; J., 1919, 187A.
[45] Monatsh. Chem., 1918, 39, 865; J., 1919, 227A.
[46] Chem. Umschau, 1916, 23, 1; J., 1919, 227A.
[47] Chem. Umschau, 1919, 26, 65; J., 1919, 471A.
[48] J. Soc. Dyers and Col., 1919, 35, 148; J., 1919, 472A.

on the constituents of French and American rosins that they probably exist in the main as anhydrides, and that hydration is a preliminary step towards the crystallisation of the resin acids, such hydration being evidenced by the whitening of surfaces varnished with rosin when subjected to the prolonged action of water.

The constitution of colophony is discussed critically by L. Paul.[49] The results are described of the addition to colophony solutions of hydrochloric acid, sodium chloride solution, and alcoholic lead acetate. The colloidal properties of colophony compounds and their changes are ascribed to a special " holding power " characteristic of resinous compounds, with the apparent formation of new chemical substances. In virtue of this " holding power " resinous substances often form well crystallised compounds with hydrocarbons. True resinous substances pass into the crystalline condition, whereas the pseudo-resin substances are non-crystallisable. The colophony substance, in consequence of its colloidal nature, is a " living substance " until its colloidal water is used up, this leading to a labile equilibrium, a condition probably realised in amber.

F. A. Richter [50] extracts the fat and resin, with a yield of about 10%, from conifer needles, after preliminary treatment with boiling water.

A. Grün and R Winkler [51] have studied the action of sulphuric acid on colophony. In one treatment the rosin, in petroleum spirit solution, was exposed at --5° C. to the action of the strong acid for 6 hours, and the product obtained after removing the mineral acid and solvent. In another treatment the colophony was subjected to esterification by methyl alcohol and sulphuric acid. The products of these treatments were compared analytically with the original colophony. It is concluded that the action of sulphuric acid in the first treatment leads to the production of about 64% of the inner ester of a hydroxy acid, thus: $C_{19}H_{30}(OH)COO.C_{19}H_{30}COOH$. The formation of the inner ester is analogous to the formation of diricinoleic acid from the sulphuric acid ester of ricinoleic acid, the sulphuric acid combining with the double linkage and the product then being decomposed by water.

O. Aschan and K. E. Ekholm [52] have obtained a new resin acid from sulphite-cellulose waste liquor. R. Tsuchihashi and S. Tasaki [53] describe some resins from *Liquidamber Formosana*.

H. G. Smith [54] describes the properties of a shellac-like resin to be extracted by alcohol from the outer bark of the *Maleleuca uncinita*, the yield being 20-25%.

[49] *Kolloid Zeits.*, 1919, **24**, 95, 129, 165 ; *J.*, 1919, 545a.
[50] Ger. Pat. 311291 ; *J.*, 1919, 546a.
[51] *Chem. Umschau*, 1919, **26**, 77 ; *J.*, 1919, 589a.
[52] *Finska Kemistsamfundets Meddel.*, 1918 ; *J.*, 1919, 646a.
[53] *J. Chem. Ind. Tokyo*, 1919, **22**, 288 ; *J.*, 1919, 646a.†
[54] *J. Proc. Royal Soc. N.S. Wales*, 1917, **51**, 232 ; *J.*, 1919, 606a.

A new source of turpentine oil and resin in India is the Indian frank-
incense or olibanum, *Boswellia serrata*; the yield and characteristics
are described.[55]

DOPES AND CELLULOSE VARNISHES.

The intensive effect of war is seen in the developments in the manu-
facture of dopes and aeroplane varnishes. H. A. Gardner [56] reviews
the constitution of war time dopes, and gives the following as a typical
composition of solvent : Methyl acetate 60, methyl ketone 10, benzene
15, acetone 10, diacetone alcohol 5 ; 1 gallon of this mixed solvent is
used to dissolve 7-9 oz. of cellulose acetate and 1 oz. of triphenyl
phosphate, with addition of small quantities of such compounds as
benzyl acetate, benzyl benzoate, or urea. In the departure from the
earlier types of dopes the main aims have been to reduce the toxic
qualities of chlorinated solvents, and to leave finally a flexible coating,
impervious to water, and non-inflammable. The replacement of cellu-
lose nitrate by the acetate or other ester is an obvious step, but the
ingenuity of inventors mainly finds expression in the complexity of the
organic solvents, and in the introduction of small portions of non-
volatile organic constituents. The patents taken out are too numerous
to be noticed here ; references to them will be found distributed
throughout the *Journal* for 1919.

ANALYTICAL OR EXPERIMENTAL OBSERVATIONS

W. T. Pearce [57] deals in two papers with the estimation of the con-
stituents of oil varnishes. The first paper describes the identification
of China wood oil and other fatty oils in varnishes. When China wood
oil alone is used in partial replacement of linseed oil, the refractive
index of the fatty acids is found to be more effective than the poly-
merisation test laid down by Boughton. In the second paper Pearce,
starting with carefully synthesised varnishes, deals with the estima-
tion of the constituents analytically, the results being given under the
headings of rosin (colophony), ordinary gum resins, fatty oils, and
thinners with separate estimation of benzine. The rosin is determined
by McIlhiney's method, Wolff's mode of esterification being adopted
instead of Twitchell's. Boughton's [58] procedure for the estimation
of gum resins and oils, though slow, is found to be satisfactory. The
illustrative results are good. The estimation of certain pigments is the
subject of a paper by G. J. Hough,[59] *e.g.*, cuprous copper in copper
paints, lime in white lead, chromium in chrome yellow and in mixed

[55] *J.*, 1919, 85R.   [56] *Circ.* 65, *Paint Manufrs. Assoc. U.S.*; *J.*, 1919, 545A,
[57] *J. Ind. Eng. Chem.*, 1919, 11, 121, 200; *J.*, 1919, 226A, 263A.
[58] *U.S. Bureau of Standards, Tech. Paper* 65; *J.*, 1919, 263A.
[59] *J. Ind. Eng. Chem.*, 1919, 11, 767; *J.*, 1919, 914A.

pigments. H. C. S. de Whalley [60] judges the viscosity of varnishes by dipping microscope slides of fixed dimensions in the varnish, the latter being at a standard temperature. The slide is then withdrawn, allowed to drain a definite time, and the increase of weight noted, this being taken as proportional to the viscosity of the varnish. A. de Waele [61] deals with the determination of thinners in oil varnishes, and in another paper [62] with the permeability of paint and varnish films; he calls attention to the extraordinary absence of bloom and chalking of varnishes made with tung oil, when immersed in water. H. Wolff [63] has experimented with varnished surfaces exposed to water, the water being varied with respect to dissolved air and oxygen. He concludes that any action which attended the experiment was due solely to the water, and not to the dissolved gases. H. A. Gardner [64] finds the compounds of the rare earths to yield very opaque pigments, with hiding power comparable with that of lead and zinc pigments. A radium salt when mixed with a pigment-base like zinc sulphide and a varnish, yields a paint with a soft greenish glow of great durability, much superior to ordinary luminescent paint.

The U.S. Bureau of Standards [65] suggest that for the detection of soya bean oil in linseed oil the figure for the hexabromide will be found much more effective than the iodine value. For pure linseed oil the value for the hexabromide lies between 45·6 and 46·9, whilst the upper limit for the hexabromide from soya oil is about 5, and averages 2·2. A. Grün and J. Janko [66] discuss the variable results for the iodine value of colophony, according to the reagent used and time of exposure, the results being complicated by the joint substitutive and additive effects. Miss E. M. Taylor [67] finds that if instead of Wijs' solution, a solution of iodine tribromide in chloroform be used, turpentine reacts so as to give a distinct resting stage at a figure for absorption equal to 4Br for $C_{10}H_{16}$. The stage is reached almost instantaneously. E. Fourneau and M. Crespo [68] suggest the use of alcoholysis in the study of balsams, e.g., by boiling with alcohol containing hydrochloric acid. The resins are not attacked. T. L. Crossley [69] discusses the different methods of determining the melting points of resins. In the examination of oil varnishes, and after the removal of the thinners by steam distillation, A. de Waele [70] recommends the addition of small quantities of a mixture

[60] Analyst, 1919, 44, 288; J., 1919, 688A.
[61] Analyst, 1918, 43, 408; J., 1919, 46A.
[62] Oil and Col. Chem. Assoc.; J., 1919, 394R.
[63] Farben Zeit., 1919, 24, 961; J., 1919, 781A.
[64] Chem. Trade J., 1919, 64, 508.   [65] J., 1919, 437R.
[66] Chem. Umschau, 1919, 26, 20, 35; J., 1919, 506A.
[67] Analyst, 1919, 44, 401; J., 1920, 72A.
[68] Bull. Soc. Chim., 1919, 25, 386; J., 1919, 688A.
[69] J. Ind. Eng. Chem., 1919, 11, 52; J., 1919, 186A.
[70] Analyst, 1918, 43, 408; J., 1919, 46A.

of benzene (3 parts) and alcohol (1 part).   The water locked up in the
residue is thereby liberated, and can be readily removed by boiling out,
leaving the non-volatile constituents in a condition for further examina-
tion.

MISCELLANEOUS.

Y. Shinosaki[71] gives the properties of Japanese turpentine from *Pinus
thumbergii*. It yielded 73% of colophony and 23% of essential oil.
The characteristics of the latter are described.   O. Aschan[72] deals
with the terpenes and resinous constituents of Finnish turpentine.
The content of iron, silica, and alumina in resins etc. is given by M.
Gonnermann.[73]   A useful review of the paint and varnish industry is
given by A. de Waele.[74]   W. A. Allsebrook[75] read an interesting paper
before the Oil and Colour Chemists' Association on monoazo dyestuffs
for lakes and pigments.   A history of the manufacture of floor cloth
and linoleum has been compiled by M. W. Jones,[76] and the distinguish-
ing features between floor cloth, kamptulicon, linoleum, and corticine
are explained.   J. Alexander[77] has taken out a patent for producing
pigments in finely divided condition.   The solutions before interaction
each receive a protective colloid, *e.g.*, in the preparation of lithopone,
gelatin is added to both the barium sulphide and the zinc sulphate
solutions.   Specifications of quality for paint oils and pigments become
more numerous, especially in America- the home of standardisation—
and attention may be called to those for linseed oil, raw, refined, and
boiled, prepared by the U.S. Government Inter-departmental Com-
mittee on Paint Specification Standardisation.[78]   In virtue of its
hygroscopic power glycol is used by T. Goldschmidt[79] instead of
glycerol in making printing and stamping inks.

[71] *J. Chem. Ind. Tokyo*, 1918, **21**, 763 ; *J* , 1919, 21A.
[72] *Finska Kemistsamfundets Meddel.*, 1918 , *J.*, 1919, 656A.
[73] *Biochem. Zeits.*, 1919, **95**, 286 ; *J.*, 1919, 729A.
[74] *J.*, 1919, 2R.   [75] *Chem. Trade J.*, 1919, **65**, 573.
[76] *J.*, 1919, 26T.   [77] U.S. Pat. 1259708 ; *J* 1919 263A
[78] *J. Ind. Eng. Chem.* 1919, **11**, 903.
[79] Ger 'Pat. 309911 ; *J.*, 1919, 379A.

INDIA RUBBER.

By D. F. Twiss, D Sc , F.I.C.,

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THE outstanding feature of the year's literature is the increase in the number of published investigations on the immediate and subsequent changes caused by vulcanisation. Reference to these investigations will be found in the appropriate section of the report. It is, however, almost impossible to resist a conviction that the published investigations lag considerably behind the actual state of knowledge in technical practice, and are consequently liable to give a wrong impression of the scientific standard in the rubber industry.

A very interesting historical account of the rubber industry and a review of its present position have been given during the year by B. D. Porritt.[1] In producing 70–80% of the world's total supply of raw rubber within the empire, Britain holds a predominant position, but as a consumer it is a bad second to the United States, whose demand for some year. has approximated to two-thirds of the world's output, and even previous to the war reached approximately one-half of the total.

Much interest attaches to the action of the British Association for the Advancement of Science in its recent institution of periodic reports on colloid chemistry and its industrial applications. Two reports have appeared so far, in 1917 and 1919 respectively ; only in the former is rubber given special mention, a section by H. P. Stevens presenting a brief general summary of the chemistry of rubber from the industrial point of view, but the progress and discoveries made in other branches of colloid chemistry should prove of considerable service to the rubber technologist in indicating likely directions for fruitful research.

STATISTICS

On account of the difficulties and restriction of shipping, the world's output of rubber for 1918, as measured by the exports from the rubber-growing districts, fell short of the estimate,[2] although the steady increase in the area under plantation rubber was maintained : the decrease in the total quantity exported was the greatest since the foundation of the plantation rubber industry. During 1919 the transport conditions have been such as to render possible the delivery o

[1] *J Roy. Soc. Arts*, 1919, 67, 252.   [2] *Ann. Repts.*, 1918, 3, 299.

the surplus from 1918, and the combined total for the two years promises
to exhibit a normal increase. The approximate figures are given in
the following table,[3] whilst the general trend of the variation in the
annual production (as distinct from the annual shipment) is shown in
the corresponding diagram (Fig. 1). This emphasises in a striking
manner the remarkable progress of plantation rubber and, inferentially,
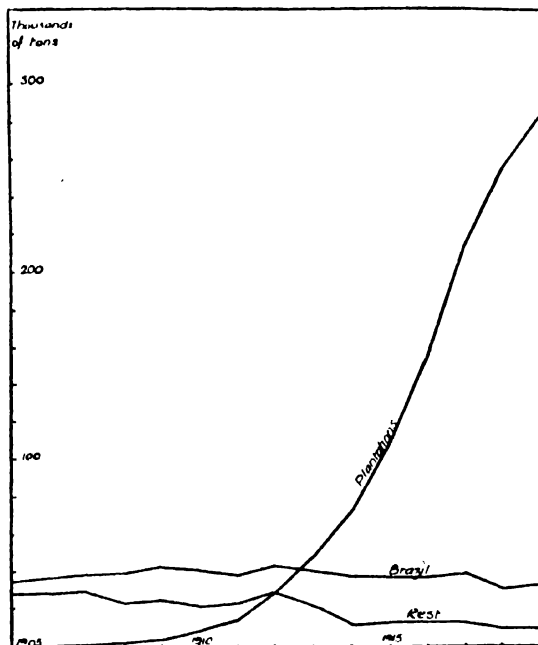
FIG. 1.—ANNUAL PRODUCTION OF RUBBER SINCE 1905.

the overwhelming proportion of *Herea* rubber (plantation and Brazilian)
in the total.

Year.	Plantation.	Brazil	Rest.	Total (in tons).	Percentage of increase or decrease
1913 . .	47,618	39,370	21,452	108,440	+ 9·6
1914 . .	71,380	37,000	12,000	120,380	+11·0
1915 . .	107,867	37,220	13,615	158,702	+31·8
1916 . .	152,650	36,500	12,448	201,598	+27·0
1917 . .	213,070	39,370	13,258	265,698	+31·1
*1918 . .	200,950	30,700	·9,029	241,579	— 9·0
†1919 . .	339,000	33,000	10,000	382,000	+58·1

* Amount shipped.   † Estimated; includes 55,000 tons from 1918.

[3] " *World's Rubber Position*," Nov. 1919 (W. H. Rickinson & Son, London).

LATEX.

Specific Gravity.

The further prosecution by O. de Vries of his investigation of the effect of various conditions of tapping on the characteristics of *Hevea* latex [4] has led to a closer examination of the relationship existing between the specific gravity and the proportion of rubber present. The importance of this matter is obvious from the common use of the hydrometer on the plantation for the determination of the rubber concentration of the latex. As had been shown by earlier experiments,[5] the hydrometer and its special modifications, the " metrolac " and " latexometer," do not invariably yield accurate results, and the observed errors were frequent and of considerable magnitude. Other investigators had previously suggested that the relation between the specific gravity and the rubber content of the latex is not a simple linear one,[6] and the earlier results of de Vries had led to a belief that the specific gravity of the undiluted serum might be so variable as to make it have an important disturbing influence on the specific gravity of the latex. There are many possible openings, however, for the unauthorised and even unintentional introduction of water into the latex before it is received at headquarters, and apart from this there is an obvious danger that previous to coagulation, or during this process, the aqueous serum may undergo alteration by chemical decomposition. By repetition of the earlier experiments, with careful laboratory supervision in order to ensure the exclusion of " foreign " water, O. de Vries has been able to show that the earlier observation must have been due to accidental dilution ; the serum of latex collected under such different conditions as caused considerable variation in the rubber content, possessed a specific gravity ranging at the widest from 1·0226 to 1·0170, the corresponding figures for total solids and ash per 100 c.c., ranging from 4·5 to 3·6 grms. and from 0·6 to 0·8 grm. respectively. The specific gravity of the serum therefore can introduce but little disturbing effect in the specific gravity of the latex. Although the results also suggested a slight inconstancy in the specific gravity of the rubber, the values did not deviate far from an average of 0·913. Consequently even when the conditions cause a considerable fluctuation in the rubber content of the original latex, the points obtained on plotting the percentage of rubber against the specific gravity of the latex lie entirely within a narrow strip bordering the straight line AB (Fig. 2), the direction of which is fixed by extreme points C and D,

[4] *Ann. Repts.*, 1918, **3**, 301.
[5] O. de Vries, *Comm. Centr. Rubber Stat., Buitenzorg*, 1918, **2**, 454 ; 1917, **1**, [iv.], 53 ; also 1919, **3**, 207.
[6] *E.g.* G. Vernet, *Caoutchouc et Gutta Percha*, 1910, **7**, 4558 ; **J.**, 1910, 1464.

representing the mean specific gravity of the serum and rubber respectively.[7]

It is then possible to apply the curve AB to determine approximately the percentage of rubber from a knowledge of the specific gravity of the undiluted latex. Addition of water to a latex of composition and specific gravity represented by a point X will cause an alteration in specific gravity as indicated .by the line XY.
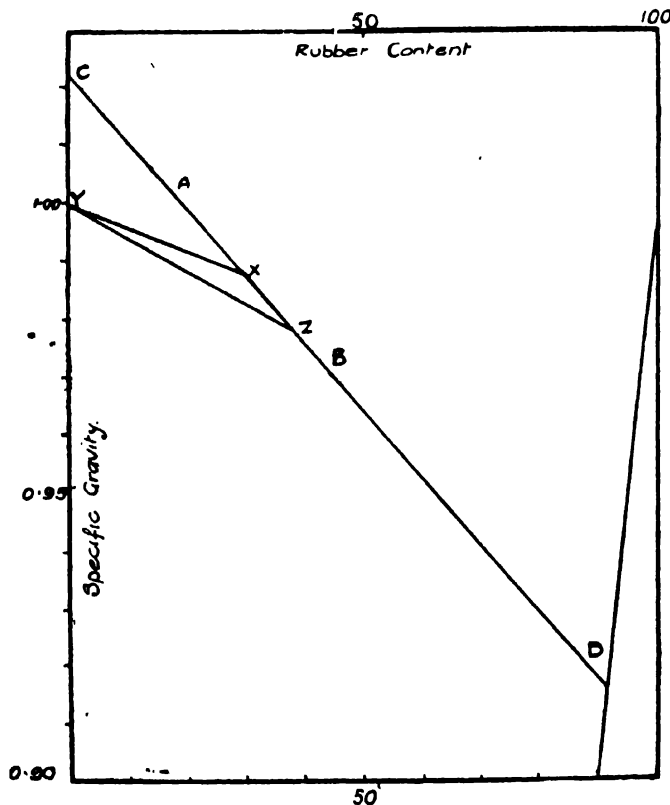
FIG. 2.*—SPECIFIC GRAVITY AND RUBBER CONTENT OF LATEX.

The scale of the " metrolac " and " latexometer " for the examination of mixtures of latex and water corresponds with the line YZ, and

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[7] O. de Vries. *Comm, Central Rubber Stat., Buitenzorg,* 1919, **3**, 183 ; *India-rubber J.,* 1919, **58**, 81 ; *J.,* 1919, 590A.

* The oblique line to the right hand of the diagram is explained by the rubber content being expressed in grms. per 100 c.c. and not in percentage by weight.

therefore appears to have been constructed for an original latex con
taining 37·5% of rubber and having sp. gr. 0·9775.[8] Being adapted to
this special case, these instruments cannot give accurate readings
with mixtures derived from original latex of any other rubber content
Observations in Java, indeed, demonstrate that the rubber content, as
estimated by such hydrometric readings, is too low and quite commonly
only 70–80% of the real percentage. It must be remembered, how-
ever, that if the proportion of rubber in the bulked undiluted
latex on an estate is fairly constant, although diverging from the postu-
lated standard expressed by the point Z, the instruments, whilst
giving a numerically incorrect reading, may be of considerable assist-
ance in adjusting all latex to a uniform concentration before coagula-
tion. In view of the difficulty of ensuring the complete exclusion of
additional water, the determination of the actual rubber content of
latex is most satisfactorily made by trial coagulation.[9] In connection
with the above research it is of interest to note that some doubt has
recently been expressed as to the advantage generally believed to
accrue from the dilution of latex to a standard concentration before
coagulation.[10]

Other Variability in Latex.

Other experiments of de Vries show that the change of tapping
surface in ordinary estate routine practice does not constitute a cause
of serious variability in the latex or in the rubber, although such varia-
bility certainly is introduced in the opening of a new cut or the re-
opening of a cut after an interval of rest.[11]

An examination of the latex from more than a thousand *Hevea* trees, in
their third year of tapping, on a seven-year-old plantation yielding 360
lb. of rubber per acre per annum, also revealed wide differences in the
rubber content, which ranged from 23% to 55%, the mean being
36·58%.[12] The average yield of rubber was 7·12 grms. per tree per day
(5·49 lb. per annum), the extremes being approximately 1·0 and 42·8 gms.
respectively, thus demonstrating the possibility of improving rubber
yields by seed selection. There was no obvious relation between the
yield of latex and the concentration, nor any general connection between
the girth of a tree and its yield. Observations extending over more
than a year demonstrated that a high percentage of rubber in the latex

  [8] The table of specific gravities given by B. J. Eaton (*Agric. Bull. Fed. Malay
States,* 1914, **2**, 314) is based on a similar scale.
  [9] The optical instrument designed by G. van Iterson (*Comm. Netherland Govt.
Inst. for Advising the Rubber Trade,* 1917, i, 18), for the estimation of rubber in
latex, cannot yet be considered successful in practice (*Indiarubber J.,* 1919, **56**,
217).   [10] *Indiarubber J.,* 1919, **57**, 756.
  [11] O. de Vries, *Comm. Centr. Rubber Stat., Buitenzorg,* 1919, **3**, 128, 137 ; *J.;*
1919, 648A.
  [12] S. Whitby, *Indiarubber J.,* 1919, **58**, 895 ; *J.,* 1919 , 954A.

of a tree was not a fleeting phenomenon, but was a consistent characteristic, although the percentage naturally suffered slight variations with changes of the weather.

RAW RUBBER

Molecular Condition.

Various matters have served to draw attention to the problem of the molecular condition of rubber. The production of synthetic rubber of the same elementary composition as highly purified natural rubber and of similar appearance, although differing in important factors (see p. 344), naturally arouses the question as to the molecular magnitude of rubber and the possible heterogeneity of its nature. The existence of the uncertainty is emphasised by the results of C. D. Harries in converting rubber into its ozonide, $C_{10}H_{16}O_6$, which appeared to be identical in all respects with that derived from gutta-percha. Harries [13] was forced to the conclusion that the $C_{10}H_{16}$ nuclei of the rubber and gutta molecules are identical and that these hydrocarbons differ only in the number of these nuclei which are more or less loosely associated in their respective molecules. A similar conclusion was arrived at by W. A. Caspari from an examination of the reaction products [14] and of the respective osmotic pressures [15] of the two hydrocarbons ; the investigation further indicated the probable identity of the purified hydrocarbons of gutta-percha and balata.

From the much greater viscosity of solutions of rubber than of gutta and the relative ease with which solutions of the essential hydrocarbon constituent of gutta can be made to crystallise by dilution or cooling, giving curved needles,[16] it is likely that the gutta hydrocarbon is in a simpler molecular condition than caoutchouc. A serious obstacle, however, in the way of coming to a definite decision in such cases is the present impossibility of drawing a sharp line of demarcation between differences which are respectively to be classed as chemical and physical. As is well known, the physical properties of any sample of rubber are not constant, but undergo modification during its existence, so that if the relation between properties and time could be represented graphically, the diagram for rubber would be a curve and not a line parallel to the time axis. Samples of raw rubber of different origin would give distinctly different curves, and it is obvious that in producing synthetic rubber of satisfactory quality the double difficulty would be encountered of placing the properties not only on an appropriate curve but also on a suitable portion of that curve. The remarkable independence of the physical properties of rubber and its chemical composition is evident

13 Z. angew. Chem.. 1912, 25, 1457 ; J.. 1912, 733.   14 J., 1905, 1274.
15 Chem. Soc. Trans.. 1914, 2139 ; J., 1914, 932.
16 A. Tschirch and O. Muller. Arch. Pharm., 1905, 243, 114 ; J., 1905, 627.
A. Tschirch and E. Schereschewski, Arch. Pharm., 1905, 243, 358 ; J., 1905, 698.

in the effect of excessive mastication and even of ordinary vulcanisation in which the proportion of sulphur entering into combination seems to be disproportionately low. An even more marked example, perhaps, is that observed in R Marquis and F. Hemi's method [17] for estimating the percentage of rubber in crude samples of the unvulcanised material by shaking the chloroform solution for a few minutes with sulphuric acid ; the rubber precipitate obtained on pouring the solution into alcohol, instead of forming the usual adhesive clot, is loose and flocculent and can be easily collected and washed in the ordinary manner of filtration. Although slight chemical action might be expected under such treatment, the composition of the rubber appears to be quite unaltered.

Attention has recently been directed to another piece of evidence as to the complexity of natural rubber. Not only do crude rubber and gutta possess the characteristics of typical colloids of the emulsoid type, but the purified hydrocarbons which form their main and essential constituents have the same characteristics. The material of the rubber and gutta hydrocarbons must therefore be regarded in each case as consisting of at least two varieties forming the two necessary phases for an emulsoid colloid. The marked change in rigidity and opacity which rubber and gutta undergo, the former when thawed from a " frozen " condition by warming to the neighbourhood of 10° C., and the latter when warmed to the vicinity of 80° C., appears to be distinct evidence against homogeneity.[18] Natural rubber behaves differently towards various solvents. Whereas in benzene, masticated natural rubber dissolves to an almost clear solution, the solution in petroleum naphtha is turbid or milky ; if unmasticated sheet rubber is treated with these solvents, the rubber swells and finally passes almost completely into solution, leaving a distended and perhaps fragmentary residue the weight of which is greater with petroleum naphtha than with benzene ; a remarkable feature, however, in the latter case is that both solutions are perfectly clear and transparent. Contrary to W. A. Caspari's views,[19] the protein constituents of the rubber are not sufficient to account for the behaviour, because these are insoluble in both the solvents mentioned.[20] The deduction therefore is that natural rubber contains at least two caoutchouc constituents,[21] of which one is more soluble in benzene than in petroleum naphtha, the less soluble fraction

[17] *Bull. Soc. Chim.*, 1913. (iv.). **13**, 862 ; *J.*, 1914, 951 ; see also Utz, *Z. angew. Chem.*, 1919, **32**, 235 ; *J.*, 1919, 688A.

[18] D. F. Twiss, *J.*, 1919, 18T.   [19] *J.*, 1913, 1041.

[20] H. P. Stevens (*J.*, 1919, 192T) regards petroleum naphtha merely as a generally less effective solvent than benzene for rubber and its behaviour as differing only in degree and not in kind ; this view also appears difficult to reconcile with the above facts.

[21] See also A. Tschirch, *Schweiz. Chem. Zeit.*, 1919, 153. *Indiarubber J.*, 1919 **58**, 789.

forming a suspension, and thereby causing the turbidity in the petro-
leum solution of masticated rubber. A similar condition of complexity
can be argued 'for gutta-percha, which shows different solubility be-
haviour towards carbon bisulphide and benzene. A sample of German
synthetic methyl-rubber, recently examined by the writer, was much
more resistant than natural rubber to the action of the usual solvents,
and the solutions were in all cases clear, thus indicating a simpler
composition than natural rubber, and probably accounting, in part,
for the observed inferiority in the physical characteristics of the
synthetic product (see p. 345).

Variability in Rubber.

As is now well known, the variability of plantation rubber, in the
sense of a lack of uniformity in the readiness with which it undergoes
vulcanisation, mainly arises from previous alteration, not in the caout-
chouc constituent of the rubber, but in the accompanying " foreign "
matter. A marked advance was effected when B. J. Eaton and J.
Grantham were able to demonstrate that the chief cause of such varia-
bility lies in the unequal extent to which the protein matter of freshly
coagulated latex has undergone decomposition into simpler nitrogenous
substances before drying is completed. A general review of the work
done at Kuala Lumpur in the Federated Malay States, most of which
has been published already, and in which the above work of Eaton
and Grantham is included, has recently been published.[22]

Independent figures published in Java serve to complement the pre-
ceding publication. As the result of hundreds of tests on plantation
rubber from many estates in the Netherlands East Indies it is possible
to quote the following figures for smoked sheet and first quality crêpe
during 1917 and 1918:[23]

	Tensile strength		Slope		Time of cure		
	Average	Normal values	Average.	Normal values	Average	Normal values.	Limits
Smoked sheet :							
1917	1·10	1·36–1·45	37·2	36–38	99	85–105	65–140
1918	1·38	1·31 1·41	36·5		96	85–105	65–130
Crêpe :							
1917	1·38	1·34–1·12	35·9	35–37	119	110–125	70–150
1918	1·37	1·34–1·40	35·5		118	110–125	85–130

The standard cure for which the period and tensile strength are given is effected

[22] B. J. Eaton, J. Grantham, and F. W. F. Day. *Agric. Bull. Fed. Malay States*,
1918, **27**, 1–398; *J.*, 1919, 111A; also *Indiarubber J.*, 1919, **57**, 249. A summary
of the almost parallel investigations made conjointly by L. E. Campbell in Ceylon
and the Imperial Institute, London, under the Ceylon Rubber Research Scheme,
has also recently been published by L. E. Campbell, under the title " *Rubber
Research in Ceylon*," 236 pp., 1918 (H. C. Cottle, Colombo).

[23] O. de Vries and W. Spoon. *Comm. Central Rubber Stat.*, *Buitenzorg*, 1919, **3**,
266 *J.*, 191?, 731A.

at 148° C., with a mixing of 92½°ₒ, rubber and 7½°ₒ sulphur, and is represented by a stress-strain curve which at a load of 1·30 kilos per sq. mm. shows an elongation of 900°ₒ.

The above figures demonstrate that the smoked sheet possessed a very distinct advantage in rate of vulcanisation, and the shorter period of heating is probably sufficient to account for the slightly greater strength ; as the last column suggests, however, and as is proved by the following more detailed figures, the variability was much greater with smoked sheet.[21]

Times of Cure, in Minutes.

	< 75	75	80	85	90	95	100	105	110	115	120	125	130	135	140	>140	Total of samples.
Smoked sheet :																	
1917	4	5	8	32	45	50	51	42	18	14	10	6	5	2	3	–	295
1918	4	9	15	18	36	32	21	20	15	14	15	5	3	--	---	---	193
Crêpe :																	
1917	1	---	--	---	2	2	13	18	37	49	41	49	24	19	5	5	265
1918	--	—	—	1	1	1	1	5	15	29	28	30	10	—	--	---	731

The differences influencing the rate of vulcanisation are grouped by O. de Vries and W. Spoon as being dependent on the following factors : (1) The composition of the latex ; (2) the addition of chemicals to the latex ; (3) the chemical changes in the non-rubber constituents in the wet rubber (maturing) ; and (4) the smoke constituents and decomposition products formed by heating. Interesting figures are given illustrating the diminution in variability which accrues from the standardisation of the treatment to which the latex and the newly coagulated rubber are submitted. It may be remarked that after considerable experience of viscosity determinations with raw rubber, these authors accede to the fairly general opinion that viscosity measurements with the rubber do not provide any definite index as to the rate of vulcanisation and are of little value for assessing the properties after vulcanisation.[25]

MIXING.

State of Division of Ingredients.

The presence of mineral ingredients in a fine state of sub-division in vulcanised rubber has long been recognised as capable of imparting

[24] A somewhat similar comparison of variability in crêpe and sheet rubber is given by A. van Rossem, *Comm. Nether. Govt. Inst for Advising Rubber Trade*, 1918, **5**, 168.

[25] See also O. de Vries, *Comm. Central Rubber Stat., Buitenzorg*, 1919, **2**, 481 ; *J.*, 1919, 22A.

desirable characteristics, and a knowledge of the relative effect of the various powders forms an important part of the rubber technologist's equipment. Zinc oxide has generally been regarded as the best of its class, but during recent years its position has been threatened by the increasing popularity of amorphous carbon,[26] viz., lampblack, and especially the variety known as " carbon black " or " gas black." This is obtained by the incomplete combustion of natural hydrocarbon gases in America, where it is collected by making the flames impinge on a moving metal surface.[27] The amount of gas black used annually in rubber goods, chiefly tyres, is estimated at 20,000,000 lb. It is significant that these two outstanding ingredients, zinc oxide and carbon black, from their method of formation are necessarily exceedingly fine powders. In the case of the relatively light carbon black the smallness of the particles causes an undesirable tendency to the formation of dust during the mixing operation, and many devices have been tried to mitigate this evil. The simple moistening or damping of the powder with water or kerosene which become eliminated during the subsequent " working " of the mixing has been recommended.[28] Another proposal is to render the black more coherent by adding a binding agent such as a mixture of water with an adhesive substance,[29] or with resin oil,[30] and then to granulate the material after drying ; mere compression indeed is also sufficient to reduce the dustiness of carbon black, but it is not certain that such processes for diminishing one trouble will not give rise to other practical difficulties.

Modified Methods for Introduction of Ingredients.

Generally speaking, the finer the state of aggregation of a mineral substance the greater the strength and toughness of the rubber mixing into which it is introduced [31] ; precipitated barium sulphate is well known to be superior to the pulverised mineral barytes. Unfortunately in the drying of moist powders the particles generally become agglomerated ; also the standard method adopted for mixing the dried powders into the rubber is liable, by friction and compression, to induce additional coarseness. Powders prepared by precipitation, therefore, may be considerably depreciated in fineness before they find their

[26] *Indiarubber J.*, 1919, **58**, 19.

[27] G. L. Cabot, *8th Int. Cong. Appl. Chem.*, 1912, **12**, Section Vc, p. 13 ; see also G. P. Lashman, *J.*, 1916, 767 ; *Indiarubber World*, 1919, **59**, 250.

[28] See *Ann. Repts.*, 1918, **3**, 307.

[29] W. C. Knowlton and H. A. Hoffmann, U.S. Pat. 1286024, 1918 ; *J.*, 1919, 112A.

[30] E. L. Curbishley, Eng. Pat. 127770, 1919 ; *J.*, 1919, 545A.

[31] The advantage of fine powders relative to coarse ones is probably accounted for largely by the greater tendency of the rubber, when stretched, to separate from the larger particles. An interesting experiment in this connection has been described by H. F. Schippel, *Indiarubber World*, 1919, **61**, 20.

place in the rubber mixing. This depreciation, it is claimed,[32] can be obviated by omitting the drying operation and using all the mineral ingredients in the form of a paste with water or other liquid ; indeed the fineness of the original wet precipitated powders may then be advantageously intensified by effecting precipitation in the presence of glue. It is stated that by mixing the wet powders into the rubber, the retention of their fine state of subdivision is ensured, and their uniform dissemination is effected with a minimum of mechanical working ; the water is removed from the mixing by a subsequent drying operation. The practical difficulties in the way of such a modification of the mixing operation as applied to mineral ingredients appear to be serious ; in the introduction of colloids such as glue, however, the possible advantage to be gained by applying a soft aqueous jelly in place of the brittle dry material will readily be conceded

A somewhat similar principle to the above has been employed by D. F. Twiss for the introduction of alkalis such as potassium hydroxide or sodium hydroxide into rubber, in which they act as vulcanisation catalysts , the medium originally used was glycerol or glycol, which act as solvents for the alkali and, by carrying the latter into the rubber, effect a perfectly uniform distribution.[33] Other hydroxylic substances of feebly acidic nature such as the alcohols and phenols can serve a similar purpose.[34] In all cases it is probable that a more or less feeble compound is formed which, by subsequent hydrolysis due to moisture invariably present in the rubber, liberates the catalytic alkali *in situ.*

Plastic Ingredients " Rubber Substitutes."

The above reference to the application of glue as a rubber " filler " recalls the increasing extent to which this material is coming into use for this purpose ; it now occupies a recognised place in the trade lists of rubber chemicals, and appears to be especially popular in America,[35] where it is estimated that the rubber trade will this year consume approximately seven million pounds of glue. The invariable presence of natural protein matter in raw rubber must have prompted many rubber workers to experiment with glue and derived gelatinous masses as ingredients for rubber. Already in 1912 F. Frank and E. Marckwald [36] had examined commercial samples containing Guayule rubber

[32] R. C. Hartong, U.S. Pat. 1301693, 1919 ; *J* , 1919, 472A.

[33] *J.,* 1917, 1185.

[34] Dunlop Rubber Co. and D. F. Twiss, Eng. Pat. 125696, 1918 ; *J.,* 1919, 429A. The use of sodium phenoxide for accelerating vulcanisation has also been protected by the North British Rubber Co. and B. D. Porritt, Eng. Pat. 129798, 1918 ; *J.,* 1919, 688A.

[35] A. B. Kempel. *Rubber Age and Tire News,* 1919, **5,** 337; *Indiarubber J.,* 1919, **58,** 425

[36] *Gummi-Zeit.,* 1912, **26,** 1499; *J.,* 1912, 693.

diluted with a so-called " fish rubber," which proved to be gelatin imperfectly hardened by formaldehyde. Very few definite results, however, appear to have been published in connection with gelatin as a filler. Experiments with small percentages of casein, which might be expected to give results very roughly comparable with those of the corresponding glue mixings, particularly as to the rate of vulcanisation, have been made by B. J. Eaton, J. Grantham, and F. W. F. Day [37]; undecomposed casein caused a slight deterioration in the tensile strength of the vulcanised mixing and did not appreciably affect the rate of vulcanisation; decomposed casein, prepared by allowing a paste to putrefy with exclusion of air and then drying, produced a distinct accelerating effect in the vulcanisation process, whereas casein decomposed under aërobic conditions was less effective in this respect. The greater uniformity of mixing which should be possible with glue would, however, lead to the expectation of more attractive mechanical qualities than were observed by the above investigators with mixings containing casein.

The great variety of substances which have been and are still commonly applied to replace or supplement the rubber in some technical mixings is made evident by a perusal of lists of so-called rubber substitutes. A fairly exhaustive enumeration made recently [38] includes raw oils, " vulcanised " oils, sulphonated oils, waxes, pitches, natural and synthetic resins, various forms of cellulose, insoluble metallic salts of the fatty acids, protein substances, etc. Such materials, however, in many cases are not mere substitutes for rubber, but are selected with a view to imparting desired characteristics.

VULCANISATION.

Sulphur.

Marked advance has been made recently in our knowledge of the common vulcanising agents and has indicated a direction for further research in connection with vulcanisation.

Ever since the discovery of vulcanisation the power of the vulcanising agent to exist in allotropic forms has exerted a fascination for the rubber chemist; indeed the first theory of vulcanisation attributed the observed changes to a parallel conversion of the rubber into an allotropic form,[39] and strikingly resembles the more modern exclusively physical view of vulcanisation.[40] for which there are now, however, few adherents.

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[37] *Agric. Bull. Fed. Malay States*, 1918, **27**, 84.

[38] F. Dannerth, *Scientific American*, 1919, **121**, 8; also A. H. King, *Chem. and Met. Eng.*, 1918, **18**, 630.

[39] W. T. Brande, 1852. See " *Personal Narrative of the Origin and Progress of the Caoutchouc or Indiarubber Manufacture in England*," p. 134 (1857), by T. Hancock (Longman).

[40] W. Ostwald, *Z. Chem. Ind. Koll.*, 1910, **6**, 136; **7**, 45; *J.*, 1910, **890, 891**.

The temperature of vulcanisation is such that probably only the allotropy of molten sulphur need be considered. In the liquid state the chief recognised modifications are $S\lambda$ corresponding with rhombic or octahedral sulphur, $S\mu$ corresponding with insoluble amorphous sulphur, and $S\pi$ a more soluble form than the others, but less stable in the solid state.[41] When pure crystalline sulphur is melted the first product is $S\lambda$, which immediately begins to undergo partial conversion into $S\pi$ and $S\mu$ until an equilibrium mixture is formed in which the proportions of the constituents depend on the temperature. In vulcanisation experiments with ordinary crystalline sulphur and insoluble sulphur the results are so closely similar that the writer was led to the opinion that no appreciable difference existed between the rate of vulcanisation[12]; this opinion has been confirmed by further and more comprehensive results obtained using two high grades of sulphur, one entirely soluble in carbon bisulphide and the other insoluble to the extent of 65%; the mixings contained 8.5% of the sulphur with 91.5% of smoked sheet rubber and were vulcanised at 50 lb steam pressure, or $147.5°$ C.

	Period of Vulc.n.		Tensile strength.	Final elongn	% Elongn at 0.5 k	Residual free S
A. Soluble	70	minutes	1.29	892	733	5.76
sulphur	80	,,	1.31	850	663	5.08
	90	,,	1.19	850	615	4.68
	100	,,	1.09	749	602	1.05
B. 65% insol-	70	,,	1.21	881	736	5.80
uble	80	,,	1.38	869	680	5.22
sulphur	90	,.	1.37	825	611	1.39
	100	,,	0.92	718	596	3.80

These results are in satisfactory accordance with the observation that when heated to melting, and therefore at ordinary vulcanisation temperatures, $S\mu$ undergoes almost immediate conversion into a mixture of $S\lambda$ and $S\pi$.[13] Another reason for believing that $S\mu$ is not likely to be a serious factor in ordinary vulcanisation is that its formation in melted crystalline sulphur does not occur to a serious extent below $170°$C.[41] On the other hand $S\pi$ is formed at the melting point of sulphur to the extent of approximately 3%, rise of temperature favouring its further formation. If $S\pi$ exerts a controlling influence in vulcanisation, its increasing proportion with rise of temperature should give rise to an abnormally high temperature coefficient for vulcanisation, which,

[41] A. H. W. Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 824.

[12] D. F. Twiss, *J.*, 1917, 787.

[13] E. Beckman and C. Platzmann, *Z anorg Chem*, 1918, **102**, 201. E. Beckmann, R. Paul and O. Liesche, *ibid.*, 1918, **103**, 189.

[44] A. M. Kellas, *Chem. Soc. Trans.*, 1918, **113**, 903.

however, is contrary to observation.[45] It is, therefore, unlikely that
$S\pi$ can have a predominant influence in vulcanisation, and probably
$S\pi$ and $S\lambda$ do not differ seriously, if at all, in vulcanising effect. The
remarkable parallel between the influence of alkaline substances on
the rate of vulcanisation and on the rate of attainment of equilibrium
between the above forms of sulphur appears therefore to be merely
a coincidence.

In connection with the above considerations interest attaches to a
recent description of a new method of vulcanisation [46] which is effective
even at the ordinary temperature ; the description includes only the
practical details and the actual form in which the sulphur reacts is left
undecided. The process involves the successive, and if necessary
repeated, application of sulphur dioxide and hydrogen sulphide to the
rubber, which may be used either as thin sheet or as solution. In the
latter case, after complete or partial saturation with sulphur dioxide
and subsequent treatment with hydrogen sulphide, the solution rapidly
increases in viscosity and finally gelatinises ; on drying, the gelatinous
mass shrinks to a mass of vulcanised rubber. As, under comparable
conditions, rubber may be chemically affected by sulphur dioxide
alone,[47] the above process, contrary to the suggestion of its author,
may not be dependent on a direct combination of rubber with elemen-
tary sulphur formed by the interaction of the two gases.

Theories of Vulcanisation.

A theory of vulcanisation postulating the existence of an especially
reactive form of sulphur has recently been advanced by H. J. Prins[48] ;
under the influence of the sulphur the rubber molecules are believed to
become activated and undergo simple polymerisation, whilst concur-
rently the sulphur in the presence of the unsaturated rubber molecules
becomes converted into an active form ; vulcanisation proper then
occurs by a further polymerisation of the rubber molecules with simul-
taneous fixation of sulphur. In some respects these views recall
H. Erdmann's theory [49] of vulcanisation, but possess a slight advantage
in providing an explanation of the looseness of the relationship between
the physical properties of the vulcanised rubber and the extent of the
combination with sulphur.

[45] D. Spence and J. Young, J., 1913, 1120 ; G. D. Kratz, Indiarubber J., 1916,
51, 601 ; J., 1916, 643 ; A. van Rossem, J., 1918, 476A ; A. O. Bourn, India-
rubber J., 1913, **45**, 120 ; J., 1913, 760. O. de Vries, Comm. Centr. Rubber
Stat., Buitenzorg, 1915, **1**, 31.

[46] S. J. Peachey, Eng. Pat. 129826, 1919 ; J., 1919, 688A.

[47] G. Fendler, Gummi Zeit, 1904, **19**, 41 ; J., 1904, 1103. F. W. Hinrichsen
and K. Memmler, Kautschuk und seine Prüfung, p. 53.

[48] Chem. Weekblad, 1919, **16**, 64 ; J., 1919, 152A.

[49] Annalen, 1908, **362**, 133 ; J., 1908, 934.

A. Dubosc has published an extension of his conception of the vulcanisation process, and of the manner in which the rate can be influenced by various catalytic substances; unfortunately there is still the disadvantage that the statements are almost entirely unsupported by evidence.[50] Accelerated vulcanisation is regarded as due to the chemical effect of colloidal sulphur arising from the interaction of hydrogen sulphide and sulphur dioxide inside the rubber mass; these gases respectively are supposed to be formed from the sulphur ordinarily present, by the action of the natural resins and the metallic oxides in the mixing. In addition it is postulated that nitrogenous accelerators by interaction with sulphur are capable of producing thiocyanic acid, each molecule of which then undergoes chemical condensation with two rubber molecules, thereby exerting a strengthening effect or " vitalising action " on the rubber According to this view, therefore, a vulcanisation catalyst may be effective by increasing the formation of sulphur dioxide and hydrogen sulphide, and also by giving rise to thiocyanic acid, thereby inducing ' vitalisation "

Sulphur Chloride.

An investigation of this vulcanising agent has proved of interest in connection with cold vulcanisation As has been remarked by several observers, the proportion of sulphur to chlorine in a cold vulcanised rubber frequently, if not generally, exceeds that expected from a simple addition to of S_2Cl_2 molecules. It is probable that this is due, at least in part, to a decomposition of a little sulphur chloride by moisture, which is invariably present to some extent, so that whilst hydrogen chloride is eliminated, an appreciable quantity of insoluble sulphur is retained in the rubber, and by the ordinary method of analysis is included with the combined sulphur [51], the gradual loss of hydrogen chloride from cold vulcanised goods, indeed must have been frequently noticed. Commercial sulphur chloride as used by rubber manufacturers, however, almost invariably contains a small excess of " free " sulphur, and G. Brum and M. Amadori have recently demonstrated that in such solutions of sulphur in sulphur chloride, partial formation of " polysulphur chlorides " such as S_4Cl_2 occurs.[52] An additive chemical reaction with such molecules will naturally give rise to products showing a ratio of sulphur to chlorine in excess of that represented by an addition of S_2Cl_2 molecules only. The observed formation of di- and tetra-sulphide compounds in the action of sulphur chloride on β-naphthol [53] probably has a similar explanation.

[50] Ann. Repts., 1918, **3**, 316; Indiarubber World, 1918, **59**, 78; 1919, **59**, 248; Caoutchouc et Gutta-percha, 1919, **16**, 9853, 9856, 9858, 9860; J., 1919, 648A.

[51] D. F. Twiss, J., 1917, 783, 788

[52] Atti R. Accad. Lincei, 1919, [v.], **28**, i 217; Indiarubber J., 1919, **58**, 129, 171.

[53] R. Henriques, Ber., 1894, **27**, 2993.

Fixation of Sulphur during Vulcanisation.

The surprising results obtained by C. D. Harries and E. Fonrobert to the effect that vulcanisation is not accompanied by any appreciable combination with sulphur, and that the sulphur can be almost entirely withdrawn, although slowly, by extraction with acetone,[54] have received further criticism. No definite description was given in the original paper as to the physical characteristics of the rubber, such as the tensile strength, but the sample examined was evidently under-vulcanised. In a repetition of the test with a mixing and conditions of vulcanisation similar to those of the earlier experiment, but using the mixing in thin sheets in order to ensure a uniform degree of vulcanisation, H. P. Stevens has found that the whole of the free sulphur, within the limits of experimental error, can be removed by continuous extraction with acetone within 50 hours, and that the remaining combined sulphur exceeds 1% of the rubber. Contrary to the view of Harries and Fonrobert, therefore, the technical effect of vulcanisation is not produced without the concurrent fixation of an appreciable proportion of sulphur.[55]

As has been shown by several independent investigations, the rate of fixation of sulphur during vulcanisation of a plain rubber-sulphur mixing containing less than 10% of sulphur is uniform until almost the whole of the free sulphur has disappeared[56]; in the case of mixings containing an accelerator, however, the rate frequently exhibits a continuous decrease as the free sulphur goes into combination.[57] Using a "technical" mixing containing rubber (100), zinc oxide (100), sulphur (5), and an organic accelerator (0·33), G. D. Kratz and A. H. Flower have investigated the possibility of maintaining a constant rate of combination with sulphur by periodically adjusting the temperature.[58] Even with a fixed temperature of 298° F., the curve representing the rate of vulcanisation was practically rectilinear up to a vulcanisation coefficient of 2·9, but by well-timed increases in temperature through the steps 285·5°, 298·0°, 302·5°, and 307·0° F., it was possible to obtain an almost rectilinear relation between the period of vulcanisation and the percentage of combined sulphur, up to a coefficient of approximately 4. At coefficients above 2·8 the product of the graded cure compared with that vulcanised to the same extent at a steady temperature was adjudged to be distinctly superior in elongation and slightly superior in tensile strength, although at lower coefficients the

[54] Ann. Repts., 1918, 3, 320.   [55] H. P. Stevens, J., 1919, 192T.

[56] Ann. Repts., 1918, 3, 313; also B. J. Eaton, J. Grantham, and F. W. F. Day, Agric. Bull. F.M.S., 1918, 27, 132; O. de Vries, Comm. Central Rubber Stat., Buitenzorg, 1915, 1, 5.

[57] G. van Iterson, Comm. Netherlands Govt. Inst. for Advising Rubber Trade, 1918, 7, 252; J., 1918, 595A.

[58] J. Ind. Eng. Chem., 1919, 11, 30; J., 1919, 151A.

difference was less marked. In the authors' opinion the best coefficient for a " technical cure " to give coincident maximum tensile strength and elongation with *Hevea* rubber should not exceed 2·8, and may be as low as 1·7, which indeed was the value for the mixing of which details are given above.[59]

Reference has already been made (p. 322) to the full summary of the experimental work on vulcanisation published from the testing station in the Federated Malay States.

Other Vulcanising Agents. •

Little has been published during the year concerning vulcanisation with agents other than sulphur or sulphur chloride[60]; the use of dinitroanthraquinone has been suggested,[61] but the results appear to show no advance on those obtained with the simpler nitro-compounds such as dinitrobenzene.

Acceleration of Vulcanisation.

In view of the importance and possibilities of the reduction of the time of vulcanisation of rubber by the application of suitable catalysts or " accelerators," the number of published investigations increases remarkably slowly, and probably gives a very erroneous impression as to the amount of experimental work which is being done in various parts of the world. To a casual reader the present state of knowledge of this section of rubber chemistry must appear almost chaotic, and the selection of an accelerator a matter of unscientific guesswork. Thiocarbanilide, according to some estimates, is the accelerator most widely used in American practice at the present time,[62] and yet in simple rubber-sulphur mixings under the customary conditions of vulcanisation its effect is slight. Apparently in order to explain its popularity, various statements, not altogether concordant, have at various times been made, such as that thiocarbanilide is particularly effective during the earlier stages of vulcanisation, that it develops its activity at much higher vulcanising temperatures than usual, or that it needs the simultaneous presence of zinc oxide or other mineral ingredients.

Mineral Accelerators.

Several workers have recently turned their attention to the relative effectiveness of the commoner inorganic or mineral catalysts. For low percentages the results generally agree in placing calcined magnesia

[59] See also H. P. Stevens, *Ann. Repts.*, 1918, **3**, 312.
[60] *Ann. Repts.*, 1916, **1**, 212 ; 1918, **3**, 318.
[61] W. A. Gibbons, U.S. Pat. 1291828 ; *J.*, 1919, 296A.
[62] C. W. Bedford and W. Scott, *Indiarubber World*, 1919, **61**, 21.

ahead of litharge in activity.[63] In this connection, however, comparison has been made between equal weights, and little, if any, attention appears to have been given to the advantage of greater bulk and consequent surface possessed by magnesia and to the fact that ordinary calcined magnesia, by its method of formation, is certain to be in a finer state of division than powdered litharge. It appears almost incontrovertible that the effectiveness of such mineral accelerators, which are only very sparingly soluble in rubber, must be largely dependent on the surface of contact 'with the rubber. Even making the unjustified assumption that the particles of litharge, by powdering, have been reduced to the same size as the magnesia particles, the superficial area of the latter powder will be approximately twice as great as that of the same weight of litharge ; when in addition one considers the great influence which a reduction of the linear dimensions has on the total surface area, the difficulty of assessing the relative intrinsic value of two mineral accelerators becomes obvious. Indeed, in comparing the effect of equal weights of litharge and magnesia in the customary manner, it would have been surprising if the relative activity had proved to fall in the reverse order.

In the case of calcined magnesia there arise further complications from the well-known existence of three main varieties produced respectively by heating " light " precipitated magnesium carbonate, " heavy " precipitated magnesium carbonate, and the mineral magnesite. It is therefore not strange that although magnesium oxide in all its modifications is superior to litharge as a catalyst, its position relative to the more effective organic accelerators has been found to vary according to the sample used. Indeed it is evident that the difficulty of comparing the intrinsic power of two accelerators will be still further increased when one is an almost insoluble powder and the other an organic substance capable of dissolving in and distributing itself uniformly throughout the mass undergoing vulcanisation (see also p. 325).

As was therefore to be expected, various samples of calcined magnesia differ seriously in activity.[64] H. P. Stevens remarks that in his earlier experiments,[65] which placed calcined magnesia above p-nitrosodimethylaniline, when applied up to a proportion of 0.7% on the mixing, a very light calcined magnesia was used, whereas G. D. Kratz and A. H. Flower, who obtained a poorer opinion of the influence of calcined magnesia, used for the comparative test a " heavy " variety, in which the particles would consequently be larger, and a basic organic accelerator which unfortunately is only described indefinitely as a condensation product

[63] H. P. Stevens, Ann. Repts., 1918, 3, 315 ; A. van Rossem, Comm. Netherlands Govt. Inst. for Advising Rubber Trade, 1918. 6, 202 ; J., 1918. 476A.

[64] H. P. Stevens, Indiarubber J., 1919, 58, 527 ; J., 1919, 782A. G. D. Kratz and A. H. Flower, Indiarubber J., 1919, 57, 827, 873 ; J., 1919, 781A.

[65] J., 1918, 156T; Ann. Repts., 1918, 3, 315.

of an amine and formaldehyde.* Their results emphasise in a marked
manner the now fairly well recognised view that when an accelerator
is used, the extensibility of the vulcanised rubber may no longer pro-
vide a trustworthy indication of the coefficient of vulcanisation.[66]
Applying a standard cure of 60 minutes at 35 lb. steam pressure to
mixings containing rubber (90), sulphur (10), and a gradually increasing
proportion of accelerator up to 1·25%, the organic accelerator in question
caused a more rapid combination with sulphur and a more rapid increase
in tensile strength, and, when more than 0·5% was present, a concurrent
increase in the extensibility as measured by the inverse of the load
necessary to produce 900% elongation.

In another experiment a mixing containing rubber 100, zinc oxide
. 100, and sulphur 5 was adopted as standard, and other mixings were
derived from it by replacing part of the zinc oxide by an equal bulk
of calcined magnesia or lime, equivalent to 5-15% by weight of the
total, so as to minimise any disturbing effect which the accelerator
might exercise as a filler. When samples were vulcanised at 50 lb.
steam pressure to what is described as the point of coincident optimum
tensile strength and elongation, the best physical properties were
obtained with approximately 10% of accelerator in each case, the
effectiveness of the accelerators decreasing in the order: light calcined
magnesia, heavy calcined magnesia, lime. With the magnesia mixings
the coefficient of vulcanisation at the "technical optimum" was
lower than that of the best plain rubber-sulphur product, the divergence
being greater with the higher percentage of accelerator; with 5% of
lime the best product also had a lower coefficient, but with 10% the
coefficient and that of the standard were almost equal.

Effect and Behaviour of Accelerators.

Kratz and Flower in their paper appear to imply that the improve-
ment in tensile strength observed when an accelerator is used is due
to the shortened period of heating necessary for vulcanisation; although
this is probably correct to some extent, it must be remembered that all
substances which expedite vulcanisation do not necessarily cause an
improvement in the tensile strength.[67]

The actual mode of action of accelerators is, as yet, little understood.
It will be recalled that the production of other accelerators from *p*-
nitrosodimethylaniline by heating with sulphur has already been recom-
mended.[68] A suggestion has now been made that all nitrogenous

* The calcined magnesia used by A. van Rossom also proved a less efficient
catalyst than *p*-nitrosodimethylaniline.

[66] See *Ann. Repts.* 1918, **3**, 311.

[67] See, for example, B. J. Eaton, J. Grantham, and F. W. F. Day, *Agric Bull.
Fed. Malay States*, 1918, **27**, 318.

[68] S. J. Peachey, Eng. Pat. 113570, 1917; *J.*, 1918, 216a.

accelerators first react with the sulphur, and that the products of this reaction form the actual catalysts.[69] If this initial reaction is really essential it is clear that the best conditions for it may not be those obtaining during vulcanisation, and the advisability of effecting it independently will be obvious. Although this method of procedure may be useful in particular cases, the evidence in favour of the generalisation is not convincing. Indeed it would be expected that if the rate of combination of rubber and sulphur in the presence of an accelerator is largely dependent on the primary formation of a compound of the accelerator with sulphur, the curve representing the progress of the combination of the sulphur with the rubber should assume a pronounced S shape, which is contrary to observation[70] (see also p. 329).

That the activity of a mixture of two catalysts may exceed the sum of the activities of its separate ingredients is a recognised chemical fact, and, indeed, the principle has already been extended by R. Ditmar to the use of catalysts in vulcanisation,[71] who has instanced calcined magnesia and litharge as examples. A special case of the same nature has been described in a claim that additive compounds of p-nitrosodimethylaniline, or its homologues, with simpler aromatic bases such as aniline, are much more effective catalysts than would be expected from the independent action of their constituents.[72]

VULCANISED RUBBER.

The Stress-Strain Curve.

As a result of the work of various rubber technologists, the representation of the effect of the degree of vulcanisation on the mechanical properties of rubber-sulphur mixings by a " stress-strain " curve has been widely adopted. A diagram of the usual type reproduces in a straightforward manner the relation between the load and the elongation for samples vulcanised over a range of periods, and therefore containing different percentages of combined sulphur. Fig. 3 gives a set of curves, each of which represents the average for a considerable number of test pieces of a 92·5 : 7·5 mixing vulcanised at 148° C.[73]; the period of vulcanisation (in hours) is stated against each curve, and the coefficient of vulcanisation for each period is given in the inset curve. A similar set of curves would be obtained with the 90 : 10 mixing, which is another common standard, but the periods of vulcanisation would be approximately only two-thirds as long for comparable

[69] Goodyear Tire and Rubber Co., Eng. Pat. 130857, 1918 ; *J.*, 1919, 731A.
[70] *Ann. Repts.*, 1918, **3**, 313.   [71] *Ann. Repts.*, 1916, **1**, 219.
[72] J. F. B. van Hasselt, Eng. Pat., 126606, 1919 ; *J.*, 1919, 640A.
[73] O. de Vries, *Comm. Central Rubber Stat. Buitenzorg*, 1915, **1**, 5 ; O. de Vries and H. J. Hellendoorn, *ibid.*, 1918, **11**, 770 ; *J.*, 1919, 188A ; O. de Vries, *J.*, 1919, 9lT.

physical results. From the diagram it is clear that a maximum of tensile strength is attained at a vulcanisation coefficient of approximately 5·0, and the customary method for determining the relative rate of cure of various rubbers is by a comparison of the periods of vulcanisation necessary for the attainment of maximum tensile strength, or for the production of the corresponding stress-strain curve.

After the shoulder is passed, the almost straight portions of the curves in any one set are parallel; the inclination of the ulterior portion of
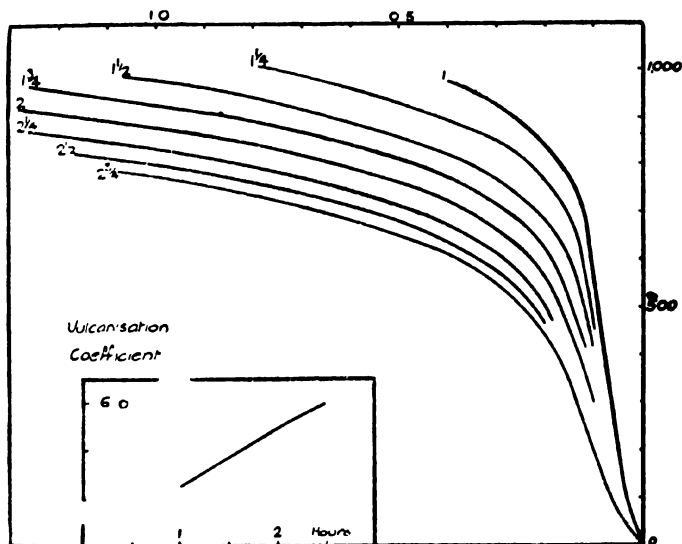
FIG. 3. EFFECT OF PROGRESSIVE VULCANISATION.

the curves relative to the horizontal axis is consequently independent of the state of cure and possesses a characteristic value dependent on the rubber used; it decides indeed the "slope" or "type" of the rubber, represented, according to the proposal of P. Schidrowitz and H. A. Goldsbrough,[74] by the quotient:

Extension (%) at 1040 grms./sq. mm.—extension (%) at 600 grms./sq. mm. ÷ 2·5.

None of the variable factors likely to occur in the ordinary work involved in the vulcanisation of rubber, other than excessive heating, has any noticeable influence on the slope of the rubber. For the different grades of plantation rubber the slope has been found

[74] *Indiarubber J.*, 1916, **51**, 505; *J.*, 1916, 550; 1919, 349r.

to vary from 34 to 51, the values for first latex crêpe and smoked sheet falling between 34 and 39·5 (see p. 322).[75] It is noteworthy that the less rapid the increase in extension of the vulcanised rubber with increasing tension towards the end of the curve, or in other words the lower the figure for the slope, the greater is the rate of increase in the initial portion. The important observation has also been made that the lower the "slope" value of a rubber the better is its resistance to suffering permanent deformation.[76]

Some years ago P. Schidrowitz drew attention to the fact that the typical rubber stress-strain curve is capable of closely approximate mathematical expression [77]; in a recent paper further details have been published.[78] If a curve be constructed by joining up the series of points which mark equal lengths, b, measured from the line AB (Fig.

FIG.4.

4) along all the possible lines that can be drawn to AB from the point P, the result is a curve ODEF, of the conchoid family, which if produced indefinitely will approach infinitely close to the prolonged line AB. The position of any point E on this curve can be represented by its vertical distances x from the line PA, and y from the line CP, and these distances x and y can be calculated from a knowledge of the lengths AP (a) and AO (b), and the angle (a) between EP and PC, the expressions for the relationship being respectively :

$$x = a \cot a - b \cos a ,$$
$$y = a - b \sin a.$$

If a new series of points is now selected with the same distances from CP, but with the distances x' from AP only a fraction n of their previous magnitude, a modified curve OGH is obtained in which the distances from CP and AP are represented by :

$$y = a - b \sin a$$
$$x' = n (a \cot a - b \cos a).$$

[75] O. de Vries and H. J. Hellendoorn. *Comm. Contr. Rubber Stat.*, *Buitenzorg*, 1917, **4**, 20 ; 1919, **15**, 269.

[76] O. de Vries and H. J. Hellendoorn, *J.*, 1917, 1258.

[77] *Rubber Industry*, 1914, 214 ; *J.*, 1915, 842 ; *Ann. Repts.*, 1916, **1**, 210.

[78] P. Schidrowitz, E. Hatschek, and H. A. Goldsbrough ; *J.*, 1919, 347T.

By this method of construction it is possible to obtain a curve almost identical with the main later portion of any rubber stress-strain curve.

Assuming OGH to be such a reproduced rubber curve the various factors are thus interpreted : a_n is constant for any set of curves for the same rubber mixing ; n decides the increase in stretch per increment of load in the typical ulterior portion of the curve ; therefore, like a_n, it varies with the type or slope ;' b is the limit of extension of the vulcanised sample, and a is regarded as representing the toughness or tenacity of the rubber.

Each individual curve in a set representing progressive cures of the same rubber-sulphur mixing can be derived from a parent curve by choosing appropriate values for b, and in every complete set there must be one curve for which b a. In the method of interpretation adopted by Schidrowitz and Goldsbrough, this curve is regarded as corresponding theoretically with an ideal balance in properties, and the condition of vulcanisation of the sample giving this stress-strain curve is termed the "perfect cure."

Using a mixture of 8 parts of sulphur with 100 parts of any variety of *Hevea* rubber and vulcanising at 286° F., it is found that the resulting "perfect cure" curves are all derivable from a parent conchoid for which a and b have a value 10·5. In all "perfect cure" curves, consequently, the trend is to a limiting extension of 10·5 times the initial length or 11·5 times if the original length is included ; this limit is attainable theoretically at infinite load.

The period of the "perfect cure" decided by this method appears commonly to be of the same order of magnitude as that indicated by methods based on the attainment of the maximum tensile strength or of the optimum product of breaking strain and final elongation, but its originators claim that its measurement is possible with greater precision.[79] When a preliminary cure has been made with a mixing of the standard composition, containing *Hevea* rubber, it is possible from the stress-strain curve of the vulcanised product to derive the values of b and n, and with the additional knowledge of the constant value of a to construct the curve for the mixing at the corresponding "perfect cure" ; from the course of this curve relative to the former the period of vulcanisation necessary can then be estimated. Schidrowitz and Goldsbrough have given figures illustrating the satisfactory use of a preliminary cure of two hours for rubbers for which the time of perfect cure ranged from one to three hours. The principle of the method, however, is so novel and arbitrary, and the evidence at present so meagre, that considerable further investigation is necessary before a safe opinion can be formed as to its practical value.[80]   Its chief advantage

[79] See also P. Schidrowitz and H. A. Goldsbrough, *Indiarubber J.*, 1916, **52**, 615.

[80] It was previously possible from the position of a single stress-strain curve to

appears to lie in its inclusion of the " type " in the considerations by which the correct cure is determined.

In all considerations of the alteration of the position of the rubber stress-strain curve with various periods of vulcanisation it is important to remember that serious disturbances may arise with mixings of relatively low sulphur content. Although stress-strain curves for mixings, containing 5 to 10% of sulphur, which have the same position, show the same contour and slope as closely as can be judged,[81] a lower proportion than 7% is not advisable on account of the possibility that during the earlier part of a long cure practically the whole of the sulphur may become combined so that during the remainder of the period the rubber is merely undergoing a heat treatment ; the rubber then begins to show an increased extensibility so that the curve slowly recedes ; with a low percentage of sulphur there is therefore a possibility of two samples with different degrees of vulcanisation being represented by one and the same curve.[82] In the presence of mineral accelerators still further complications are possible, because not only do these reduce the time of vulcanisation but any subsequent recession of the stress-strain curve may be accompanied by a marked alteration in the type or slope.[83] Doubtless the recession or reversion of the stress-strain curve on prolongation of the heating beyond the exhaustion of the free sulphur, corresponds with the softening effect which constitutes one of the chief alterations effected in the ordinary reclaiming or " regenerating " of vulcanised rubber.[84]

Ageing.

The spontaneous alteration in the physical properties of rubber after vulcanisation is also a matter of considerable importance. When kept, a sample of newly vulcanised rubber alters in such a manner that its stress-strain curve gradually becomes steeper ; the change can be expedited, for greater convenience of observation, by a slight elevation in temperature below the vulcanisation limit.[85] In 24 hours at 72° C. the modification in the curve for a 92·5 : 7·5 mixing, previously vulcanised for

decide the period necessary for the ordinary optimum cure, with an error of less than fifteen minutes ; B. J. Eaton. J. Grantham, and F. W. F Day. *Agric. Bull. F.M.S.*, 1918, **27**, 47.

[81] O. de Vries and H. J. Hellendoorn, *Comm. Central Rubber Stat. Buitenzorg*, 1918, **11**, 783 : *J.*, 1919, 188A.

[82] O. de Vries and H. J. Hellendoorn. *Indiarubber J.*, 1919, **57**, 1163 ; O. de Vries and H. J. Hellendoorn, *J.*, 1919, 93T.

[83] P. Schidrowitz and H. A. Goldsbrough, *Indiarubber J.*, 1919, **57**, 269 ; *J.*, 1919, 188A.

[84] See *Ann. Repts.*, 1918, **3**, 317.

[85] O. de Vries, *Ann. Reports*, 1917, **2**, 346 ; also W. C. Geer, *Indiarubber World*, 1916, **55**, 127 ; O. de Vries, *Comm. Centr. Rubber Stat. Buitenzorg*, 1918, **11**, 792 ; *J*, 1919, 82.

70 minutes at 148° C., was equivalent to a further period of vulcanisation of 20 minutes ; the proportion of combined sulphur was unaltered, the coefficient of vulcanisation throughout being 2·3, although the stress-strain curve of the " aged " rubber would normally have been associated with a coefficient of 3·1. The increase in tensile strength by ageing, however, is less than that produced by an extension of the vulcanisation period, so that, although the two curves follow the same course, the curve attained by ageing is shorter. The further effect of ageing at 72° C. after the first day shows a steady decrease, and is approximately the same whether the vulcanisation coefficient is 2·3, 3·1, or 4·0. On the first day, however, the effect is greatest for the least vulcanised sample. The results again demonstrate clearly the insufficiency of any one of the characteristics, vulcanisation coefficient, tensile strength, or elongation at a certain load, as an index of the state of " cure " * of a commercial sample of unknown age and history. In testing samples which have been vulcanised in the laboratory, alteration by ageing need introduce no appreciable disturbing factor because the difference observed between the physical results for similar samples tested one day, and three days after vulcanisation is equivalent only to an alteration of three minutes in the time of vulcanisation, and this, at the portion of the stress-strain diagram involved, would cause no appreciable alteration in the tensile strength.[56]

Since the completion of the last report the instability of the condition of vulcanised rubber has received further comment [57] from H. P. Stevens, who has extended his earlier observations.[58] In comparative tests with vulcanised mixings containing smoked sheet, smoked slab, pale crêpe, and smoked crêpe, the more highly cured samples appeared to undergo an increase in the vulcanisation coefficient, the average alteration for an initial coefficient of 5 to 6 being 0·5. Samples vulcanised to an immediate maximum tensile strength (" optimum cure ") corresponding with a coefficient between 4 and 5, increased gradually in strength for 10 to 15 weeks, and then rapidly deteriorated, becoming hard and " perished " within a year or so. Samples vulcanised to a coefficient of 2 to 3 improved in strength for twelve months, and then slowly weakened, but even after two years were stronger than when first vulcanised. Vulcanised rubber, however carefully vulcanisation may have been effected, evidently begins immediately to change in physical properties, and is therefore, in that respect, markedly unstable relative

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* It is desirable that the term " cure " should be restricted to the alteration in physical state, and " vulcanisation " to the chemical process of combination with sulphur. The terms are used with this special significance in this report.

[56] O. de Vries, *Indiarubber J.*, 1919, **57**, 77 ; *J.*, 1919, 82A. O. de Vries and W. Spoon, *Comm. Central Rubber Stat. Buitenzorg*, 1919, **11**, 814 ; also B. J. Eaton, J. Grantham, and F. W. F. Day, *Agric. Bull. Fed. Malay States*, 1918, **27**, 42.

[57] *J.*, 1918, 340T.   [58] See *Ann. Reports*, 1918, **3**, 312.

to raw rubber, which can be stored for many years without any sign
of depreciation either in appearance or in its characteristics after
vulcanisation. The experiments described by H. P. Stevens were
restricted to a mixing of pure rubber (90) and sulphur (10); the behaviour
of vulcanised mixings containing technical ingredients, according to a
private communication to the writer of this Report, have been found
to indicate instability of similar character, but modified in degree.

B. J. Eaton and F. W. F. Day [89] also have interested themselves in
the ageing of vulcanised rubber, but have included a closer chemical
examination of the phenomena. Crumbed samples, whether over-
cured or not, underwent a remarkable increase in weight, attaining a
maximum in about nine months. The oxidised samples contained a
surprisingly large percentage of material soluble in water, and the
aqueous extract showed the presence of sulphur in the form of sulphuric
acid or sulphate. The S-shaped form of the curves for the increase in
weight generally confirms the results of S. J. Peachey and indicates
the auto-catalytic nature of the oxidation process.[90] A greater rate
of oxidation was observed for highly-vulcanised samples. For exces-
sively over-vulcanised samples the curve for the increase in weight
followed quite a distinct course from that for less-vulcanised samples.
The behaviour in general was such as to suggest that two processes
were occurring concurrently, one involving an increase in weight, and
the other accompanied by a less effective loss in weight; it is not
surprising therefore that the apparent variation in the content of com-
bined sulphur followed no simple course. The results with uncrumbed
samples agree with those of de Vries as to the physical effect of ageing
in its earlier stages being comparable with that of an extension of the
" cure," but differ in showing a slight albeit far from commensurate
increase in the combined sulphur.[91] Although incomplete, the inves-
tigation serves to emphasise the complexity of the problem of the
ageing of vulcanised rubber, and the need for further systematic
examination.

Some interesting observations on the behaviour of vulcanised rubber
to solvents have been made by H. P. Stevens.[92] With increasing vul-
canisation the degree of swelling in benzene gradually increases, as
also does the resistance to the formation of a permanent emulsion with
excess of the solvent; a stage is finally reached at which the limit of
solubility is marked by the persistence of gelatinous flakes, and beyond

[89] J., 1919, 339T.
[90] Ann. Repts., 1918, 3, 308, 313 ; see also F. Kirchhof.' J., 1913, 799 ; G.
Huboner, J., 1913, 1163.
[91] See also Ann. Repts., 1918, 312 ; the results of H. P. Stevens (J., 1919, 196T)
agree with those of de Vries in indicating that the quantity of combined sulphur
remains practically unaltered.
[92] J., 1919, 193T. See also A van Rossem, Comm. Netherland Govt. Inst. for
Advising Rubber Trade, 1918, 6, 216.

this stage further vulcanisation causes a diminution in the swelling. Samples of a mixture of rubber and sulphur, containing 10% of the latter and vulcanised so as to contain 0.27 and 0.39% respectively of combined sulphur, when immersed overnight in benzene yielded solutions, that from the second sample being distinctly "ropy"; a sample with 0.45% of combined sulphur swelled, and on shaking broke up into gelatinous lumps, whilst a further sample with 0.51% of combined sulphur, although greatly swollen, remained whole in spite of shaking. After storage at $30°$ C for 3 months, however, the degree of solubility had decreased, and all four refused to dissolve, although each sample yielded a considerable proportion of extract to the solvent. Prolonged extraction of more highly vulcanised samples at the boiling point of the solvent gave no indication of separation of the rubber into fractions of different degrees of vulcanisation, the very considerable extract, which, after drying, refused to redissolve in fresh benzene, showing the same content of combined sulphur as the undissolved residue. Experiments on the swelling of a technical vulcanised rubber in various solvents have been made by A. Dubosc,[93] who, amongst other observations, noted that a mixture of carbon tetrachloride and carbon bisulphide possessed greater turgescent power than either constituent.

TECHNICAL PAPERS.

To the non-technical reader perhaps the most interesting part of the rubber literature is that dealing with the production of manufactured rubber goods. Descriptions of this nature, possibly in part because of the relaxation of war-time stress and restrictions, have been unusually frequent during the last year or so. As the material may be of interest for reference, a number of the subjects such as rubber sponge,[94] rubber in gas defence equipment,[95] rubbered seams,[96] typewriter platens,[97] motor-tyre rebuilding,[98] solid rubber tyres,[99] rubber shoes,[100] rubber soles,[101] and general rubber manufacture [102] may be quoted.

Permeability to Gases

Quite naturally, rubbered fabrics for airship construction and similar

[93] *Caoutchouc et Gutta-Percha*, 1919, 16, 9781, 9813, 9845, 9964 ; *J.*, 1919, 546A, 648A, 781A, 835A.

[94] A. Hutin, *Indiarubber J.*, 1919, 58, 467 A. H. King. *Met and Chem. Eng* 1916, 15, 681.

[95] C. J. Johnson. *Indiarubber World*. 1919, 59, 292.

[96] J. D. Edwards and I. L. Moore, *Indiarubber J.*, 1919, 57, 599

[97] L. E. Macfadden, *Indiarubber J.*, 1919, 57, 1147.

[98] *Indiarubber World*, 1919, 60, 552, 623.

[99] A. H. King, *Indiarubber J.*, 1919, 57, 749, 787.

[100] *Indiarubber World*, 1919, 60, 691.

[101] A. H. King, *Met. and Chem. Eng.*, 1917, 17, 72

[102] A. H. King, *ibid.* 1916, 14, 23, 71.

purposes have claimed much attention of recent years, and the results of several investigations have been made public. The method of testing the permeability of such fabrics to hydrogen as practised by the U.S. Bureau of Standards has been described,[103] and the cognate phenomena observed in the passage of gases through rubber by solution submitted to discussion. Methods involving measurement of rate of diffusion of the hydrogen by the loss in volume are relatively inaccurate, and on account of the simultaneous transfusion of air in the reverse direction give results approximating to only 70% of those obtained by methods based on the direct estimation of the hydrogen which has penetrated the rubbered fabric. The earlier observation, originating with Graham, to the effect that the permeability of rubber films increases rapidly with the temperature (see also this report, p. 344), is confirmed, although the relationship does not appear to be linear; the additional information is given that the relationship between temperature and permeability is approximately independent of the composition of the rubbered fabric, and as an approximation the permeability at 15° C. may be derived from that at 25° C. by use of a factor 0·65. The effect of alteration in the hydrogen pressure or in the hygroscopic condition of the gas during permeability tests is too small to be serious, and the fabric almost invariably attains its maximum permeability within one hour. It is noted that, in continued daily testing of one piece of fabric, a gradual decrease in permeability may occur, but a very marked decrease may be effected by heating to 75° C. for 30 minutes; during a normal day's test, however, the permeability is generally constant. The U.S. Bureau of Standards has discarded the combustion method for determining the transfused hydrogen, and the final passing of the combustion process for this purpose would probably meet with few regrets in view of the greater convenience of the physical methods of determination now available based on the alteration in the optical properties of the air using the interferometer,[104] or in its thermal conductivity using the "catharometer" of G. A. Shakespear[105]; the latter possesses the additional advantage of being readily applicable to the detection of "pinholes" in a finished rubbered envelope without the necessity of cutting the material.

A statement that the extent of diffusion of hydrogen through a good rubbered airship fabric is rarely less than 8 litres per square metre per

[103] J. D. Edwards, *Indiarubber J.*, 1918, **56**, 753, 821, 863; *J.*, 1919, 169A; see also G. Barr, *Rubber Industry*, 1914, 265; *J.*, 1915, 870; also W. Frenzel, *Chem.-Zeit.*, 1919, **43**, 530; *J.*, 1919, 835A; also J. D. Edwards and S. F. Pickering, *J. Ind. Eng. Chem.*, 1919, **11**, 968; *J.*, 1919, 895A.

[104] For a description of a portable Rayleigh interferometer for industrial use see M. Ponchon, *Chem. and Met. Eng.*, 1919, **21**, 392; also J. D. Edwards and W. Frenzel, *loc. cit.*

[105] Eng. Pat. 124453, 1916; *J.*, 1919, 393A; *Nature*, 1919, **103**, 275.

day at 25° C.[106] renders possible an interesting comparison with the result obtained with a probably thinner raw rubber membrane without any internal fabric support (this report, p. 344), and with the figures of W. Rosenhain and G. Barr for fabrics containing more than one layer of rubber.[107]

The deterioration of such rubbered fabrics on exposure to the weather has been examined, with the conclusion that the resistance to exposure is greater the higher the proportion of rubber in the fibre.[108] In view of the tediousness of natural weathering tests it is of interest to note that the device of inducing accelerated ageing by exposure to ultra-violet rays, e.g., from a quartz mercury vapour lamp, has received considerable justification by a demonstration that the effects are actually analogous[109]; the possible economy in time is evident from the fact that it is thus possible to reduce the period of weathering from 30 days to a few hours with the additional advantage that the process is under complete control

The permeability of lightly vulcanised almost pure rubber films, probably "cold-cured," to various gases and vapours has recently been brought anew to the public notice by Sir J. Dewar[110] in connection with a lecture on the problems of hydrogen and the rare gases. Using an apparatus of special design in which a rubber film approximately 0·01 mm. thick, supported between discs of copper gauze, was subjected on one side to each gas or vapour in turn, it was found that vapours of ether, chloroform, and ammonia diffused rapidly, whilst to benzene, alcohol, pyridine, and acetonitrile the rubber membrane was less permeable; the exceptionally rapid transmission of ammonia was observed as long ago as 1831 by J. K. Mitchell.[111] A film of glycerin painted over the membrane checked all diffusion.[112] A re-examination of the resistance of rubber to the passage of various gases was in good general accord with the observations of the earlier investigators.[113] and serves to extend them. In the table on page 344 the new figures are quoted in parallel with those of Thomas Graham, to the trustworthiness of whose work they form a distinct testimony; it may be stated that Graham's figures refer to experiments with films of raw rubber.

[106] J. D. Edwards and P. G. Ledig, *Indiarubber J.,* 1919, **57**, 1114.

[107] *Indiarubber J.,* 1910, **40**, 288.

[108] G. St. J. Perrott and A. E. Plumb, *J. Ind. Eng. Chem.* 1919, **11**, 138; *J.,* 1919, 408A.

[109] M. Entat, *Ann. Chem. Analyt.,* 1919, **1**, 142; *J.,* 1919, 409A, *Indiarubber J.,* 1919, **58**, 80. [110] *Proc. Roy. Inst.,* 1915, **21**, 558, 813.

[111] J. K. Mitchell, *J. Roy. Inst.,* 1831, **2**, 101, 307.

[112] See also F. Steinitzer, *Gummi Zeit.,* 1912, **26**, 1626; *J.,* 1912, 734.

[113] T. Graham, *Phil. Trans.,* 1866, **32**, 399; *J. Chem. Soc.,* 1867, **20**, 235; S. A. von Wroblewski, *Ann. Phys. Chem.,* 1876, **158**, 539; also R. Ditmar, *Indiarubber J.,* 1907, **34**, 85, 197; V. Henri *Caoutchouc et Gutta-Percha,* 1910, **7**, 4351.

Rate of Diffusion.

	Relative (Graham).	Relative (Dewar).	cc. per sq cm. per day (Dewar).
Air	1·0	1·0	2·0
Nitrogen	0·87	0·69	1·38
Carbon monoxide. .	0·98	0·94	1·88
Helium	.	1·75	3·5
Argon	—	1·28	2·56
Methane	1·87	—	
Oxygen	2·23	2·0	4·0
Hydrogen	1·79	5·16	11·2
Carbon dioxide . .	11·83	14·0	28·0

The order of diffusibility for the different gases follows no obvious law, and the absence of any simple relationship between the rate of diffusion and the other properties of the gas, which is particularly noticeable in comparing helium, hydrogen, and carbon dioxide, confirms the view that the main controlling factor is the solubility of each gas in rubber. With rise in temperature the diffusion becomes more marked, the relation between the temperature and the logarithm of the rate being representable by a straight line ; a distinct break, however, occurs in the " curve " for each gas at 0° C., and the suggestion is made that this may possibly be due to water present in some form of colloidal association as a constituent of the rubber membrane. Although this explanation may seem a little strained, it is remarkable that quite independently the importance of the presence of traces of moisture for the diffusion of carbon dioxide through rubber has been mooted.[114]

SYNTHETIC RUBBER.

Now that definite information is available as to recent progress in the production of rubber by artificial chemical processes, even those who held an unfavourable view of the likelihood of an early replacement of the natural product by synthetic material have probably been surprised at the decisive manner in which their opinion has been justified.[115] On the other hand, the attractive appearance of the raw synthetic material must have impressed those who have seen samples.

As is well known, rubber-like products have been artificially prepared by the polymerisation of various hydrocarbons represented by butadiene CH_2:$CH·CH$:CH_2, and its methyl derivatives such as isoprene C_5H_8 and 1 3-dimethylbutadiene C_6H_{10} ; the first and third naturally yield products of different elementary composition from that of pure natural caoutchouc. The polymerisation process will occur spontaneously or may be accelerated by the catalytic influence of metallic

114 V. Rodt. Chem.-Zeit., 1914, 38, 1249 ; J., 1915, 187.
115 Indiarubber J., 1919, 57, 1011.

sodium or by warming with acetic acid.[116] During the past five years
the material of greatest promise has been that derived from dimethyl-
butadiene by spontaneous polymerisation at approximately 60° C.,
the process, however, being very slow.[117] The necessary dimethyl-
butadiene was obtained by the reduction of acetone with aluminium
and sodium hydroxide, the pinacone $(CH_3)_2$:$C(OH)\cdot C(OH)$ $(CH_3)_2$ pro-
duced being subsequently dehydrated with formation of the dimethyl-
butadiene, CH_2:$C(CH_3)\cdot C(CH_3)$:CH_2. "Methyl-rubber" is obtained
from this as a very tough, colourless, transparent mass, but the pro-
perties of the material * are generally so disappointing as to confirm
G. Steimmig's statement that the molecular structure of such artificial
rubber is not identical with that of natural rubber.[118]

In a recent account of the German war-time use of this synthetic
rubber,[119] it is stated that the material was undesirably prone to
oxidation and averse to vulcanisation, but that both these disadvantages
were remediable to a large extent by the addition of organic vulcanisa-
tion catalysts such as aldehyde-ammonia or the additive compound
of piperidine with carbon bisulphide. In addition to this, however,
the methyl-rubber is remarkably resistant to mastication and to sol-
vents ; in examining a sample, the writer has observed that unless
excessively worked the material refuses to dissolve, but swells enor-
mously, and in benzene, for example, forms a jelly containing almost
15 times as much solvent as rubber. The solutions when made are
surprisingly fluid, and it is of interest that with petroleum naphtha
there is no sign of turbidity (compare p. 321).

The most satisfactory products obtained from this methyl-rubber
appear to have been vulcanites,[120] in which the unsaturated condition of
the molecule is almost entirely removed ; the production of accumulator
boxes for submarine work is stated to have been particularly successful.
Soft rubber goods such as packing sheet, rubbered fabrics, wire-insulat-
ing material, and tyres, were also made, but the very partial success
can be judged by the necessity to add "elasticators" or oily materials
for the purpose of softening the methyl-rubber. Solid tyres even then

[116] C. D. Harries, *Annalen*, 1911, **383**, 157 ; *J.*, 1911, 1073.

[117] C. Duisberg, *Z. Elektrochem.*, 1918, **24**, 369 ; *J.*, 1919, 188A ; *J Ind. Eng.
Chem.*, 1919, **11**, 819 ; *Times Eng. Suppl.*, 1919, **15**, 175.

* It will be noted that apart from its physical properties, this form of synthetic
rubber can be readily distinguished from natural rubber by the fact that it forms
a tetrabromide $C_{12}H_{20}Br_4$ containing only 66% of bromine, whereas caoutchouc
tetrabromide $C_{10}H_{16}Br_4$ contains 70·2% ; in the estimation of rubber by the tetra-
bromide method, the analytical conversion factor for methyl rubber will there-
fore be considerably greater than for natural rubber.

[118] G. Steimmig, *Ber.*, 1914, **47**, 350 ; *J.*, 1914, 269 ; also H. Staudinger,
Schweiz. Chem. Zeit., 1919, **1**, 1, 28, 60 ; *J.*, 1919, 428A.

[119] *Indiarubber J.*, 1919, **58**, 305, 348, 391, 433 ; *J.*, 1919, 730A.

[120] *J.*, 1919, 209R ; *Ann. Repts.*, 1918, **3**, 301.

exhibited a serious tendency to harden in cold weather, although they regained their pristine softness on warming, and it was necessary to issue instructions that synthetic rubber tyres were to be stored in rooms protected against frost, and that, when resting during cold weather, vehicles fitted with them were to be supported on " jacks " so as to relieve the tyres and prevent permanent local deformation ; in use also, the tyres wore away by disIntegration rather than by abrasion.   Still less success attended the attempts to produce inner tubes for pneumatic tyres.

In spite of the failure of synthetic rubber, during the exceptionally favourable period which has just passed, to rise to the expectations of its more sanguine supporters, the fact must not be overlooked that the practical trial to which it has been submitted must have served to show, more clearly than many years of academic research, the nature of the chief weaknesses in the product at present obtainable.   The most important problem appears to lie in the control of the polymerisation process, or at least in the suitable adjustment or modification of the final state of polymerisation (see p. 320) ; with a greater command of this stage of the operations it would be possible to approach more closely to the characteristics of natural rubber.

LEATHER AND GLUE.

By F. C. Thompson,

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No feature of the year 1919, within the field covered by this Report, has been more striking than the earnest effort made to bring about closer co-operation between chemists and manufacturers. There has never been a time when tanners were so fully awake to the need of utilising all available scientific knowledge, nor when chemists so much realised the necessity of taking a constructive part in the building up of leather technology. When tanners employed chemists in former years it was usually for purposes of controlling processes and testing raw materials, and the chemist himself was often content with a scope so limited. Now it seems to be almost universally realised that future discoveries are likely to come from the chemist, and that the whole industry in this country depends upon him to no small extent Many firms now employ chemists mainly for research, and at least one has a research department, whilst a British Leather Manufacturers' Research Association is in process of formation. Conferences have been held during the year in which both chemists and manufacturers have taken part, such as, for instance, the conference on the chrome tanning industry held on July 17 at the general meeting of the Society (see *J.*, July 31, 1919, 264–271T). Such gatherings are likely to be frequent in the future, and will be productive of great benefit.

Raw materials have been the cause of much difficulty and anxiety on account of scarcity and high prices, though with increased shipping facilities the scarcity was not so pronounced as during the war. Great attention is still being paid to the conservation and exploitation of natural resources. The Government has appointed a Committee [1] to deal with the warble pest in every possible way. Farmers and others are to have literature on the subject revealing the loss caused by the fly and showing them how they may do much to protect their cattle, whilst a thorough investigation is to be made of methods for eradicating the trouble. Several features of hide supply noted in last year's Report are still engaging attention, *e.g.*, the attempts to minimise preventible

[1] *J. Soc. Leather Trades Chem.*, 1919, **3**, 20,

loss and damage of hides through bad flaying, branding, cattle-tick, etc.

Natural tanning materials are being energetically exploited in India [2] and Australia, to a great,extent under Government auspices. At the Leather Trades' School, Washermanpet, Madras, experiments have been made, to find barks, etc., that can be substituted for avaram (tarwad, *Cassia auriculata*).ʳ Though this material is likely to be always the most important in South India, it is desirable to have the supplies supplemented, and good results have been obtained with the bark of *Anogeissus latifolia*. The mangroves and wattles of India are also under investigation. Much work is being done by the research station at Esociet, Central India, and by the enterprise of private firms. The leather industry in India is developing very rapidly ; and many modern tanneries are being opened in which chemists are taking an important part. In Australia private firms and the Government are investigating the natural tanning materials of the continent, and as in India, the need for cultivation is not overlooked. F. A. Coombs [3] states that although there are large supplies of tannin in the various eucalypts, much of it is of little use. Liquors prepared from *E. sideraphloia* did, not penetrate hide in ten weeks. Mallet (*E. occidentalis*) though rich in tannin is very slow, and gives a brittle leather when used alone in pit tannages. Its principal use appears to be as an adulterant. The wattles are much the best materials, being both abundant and rich in tannin.

Great efforts continue to be made to establish the chrome tanning industry more firmly in this country, and appear to be meeting with considerable success, and goods are even being exported to America. Chrome tanners especially are alive to the importance of chemistry to the industry.

HIDES, HIDE STRUCTURE, AND WET WORK.

The Seymour-Jones process for hide sterilisation by means of formic acid and mercuric chloride has been severely criticised by V. Gegenbauer,[4] who, however, did not experiment on hides but on anthrax cultures and spores. Growth was obtained after 40 days' action of a 0·02% solution of mercuric chloride in combination with as much as 5% of formic acid. Anthrax spores treated by the Seymour-Jones method proved pathogenic when introduced into guinea-pigs. It is natural to suppose that sterilisation is more difficult in the case of hides than with cultures in nutrient media, and Gegenbauer's conclusion is that for practical concentrations of acid and mercuric chloride, and reasonable times of action, the method is in no way effective. R. R. de Silva [5] proposes

[2] *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 26, 351.   [3] *J.*, 1919, 70ᴛ
[4] *Arch. Hyg.*, 1918, **87**, 289; *J.*, 1919, 429ᴀ.
[5] U.S. Pat. 1304030; *J.*, 1919, 507ᴀ.

to sterilise hides by treatment (before drying out) with copper sulphate solution. There is perhaps here a danger of a tanning effect that might render subsequent processes difficult, and which rules out many means of disinfection, such as the use of formaldehyde. The problem of hide sterilisation has proved one of the most difficult in the whole of leather technology and it is urgently necessary that further work be at once instituted, in order that a constant danger to leather workers may be removed.

A. Seymour-Jones [6] continues his work on skin physiology and gives methods for cutting hide sections. He deprecates dehydration by such means as alcohol, and proposes centrifuging, or gentle and continued compression between layers of blotting paper until the skin has the consistency of cheese. The material is then imbedded in paraffin wax of m. pt. not above 160° F., after which sections are cut, best with a rotating disc razor of stainless steel used in a Minot microtome.

W. Moeller [7] proceeds on the basis of his views on collagen structure [8] and on tanning, to put forward a theory of leather structure. There are four components normally, the collagen micells, the micells of its decomposition product, the peptiser, and the peptised tanning solution. The second and third of these may be partially or entirely absent; when present the peptiser forms a solid solution with the collagen micells. The peptised tanning solution is deposited on the collagen micells, perhaps regularly in layers of crystals. These views are not likely to be very useful to leather technologists generally until they are developed in a clearer form with the necessary experimental evidence and illustration.

Liming.

Considerable interest has been centred in practical methods of liming hides, and means for securing circulation of liquors and consequent acceleration of the process are becoming more widely adopted. In A. N. Walker's [9] process hides are hung in the lime pits, e.g., by hooks, and water is run in. The water is then agitated by means of air blown in from tubes across the bottom of the vat. When the hides are thoroughly washed the water is removed and lime-liquor run in, which is agitated by the same means for the 3-4 days necessary before unhairing. The air pressure needed is about 2 atmos., and about 15 h.-p. is needed to deal with 1000 heavy hides weekly. It is hoped to hang the hides on frames that can be lifted from the pits bodily, and transported by overhead cranes C M. Owen [10] secures

[6] *J. Soc. Leather Trades' Chem.*, 1919, **3**, 85, 107.

[7] *Collegium*, 1918, 277, 300, 333, 365 ; *J.*, 1919, 835A.

[8] See *Ann. Repts.*, 1918, **3**, 325.   [9] Eng. Pat. 124992 ; *J.*, 1919, 331A.

[10] Eng. Pat. 128451 ; *J.*, 1919, 649A.

circulation of lime liquors by means of paddles on horizontal shafts at the bottom of the pit.

Bating.

So far one of the most successful principles in making artificial bates and puers has been the use of trypsin. an enzyme which under normal circumstances is without action on true hide substance but which attacks and dissolves the elastic fibres of the skin and also any cementing proteins that remain after liming. It is noteworthy that an English product of this type, i.e., " Pancreol," now on the market, is proving very useful, and is likely to supplant the " Oropon " of pre-war days. The process of L. R. Peyrache and O. V. Bailly [11] embodies the same principle. The pancreas of animals is thoroughly extracted with successive quantities of acetone, from which it is freed by evaporation and then reduced to the finest possible powder. The same may be done with the mucus of the small intestine. The material thus prepared may be used alone or with some inert material such as cellulose, at a temperature of $30°-40°$ C., at which temperature trypsin is most active.

TANNING AND EXTRACT MANUFACTURE.

Although synthetic tanning substances are in as great demand as ever, there has been a lull in the patenting of new ones. The more obvious possibilities on the lines indicated in the last Report appear to have been fairly thoroughly worked out. A good summary of all the work on this subject is given by H. Bamberger,[12] and another by E. Nihoul[13] describes the practical aspect. E. Schwarz [14] patents tanning by means of a bath of a carbazolesulphonic acid, and this is almost the only patent of its kind to report. Iron tanning, in spite of the disappointments of the past, is still the subject of experiment, and V. Casaburi [15] describes his researches in some detail. After a review of previous work he enumerates the following points as noteworthy. (1) Normal ferrous and ferric salts have no tanning action ; (2) a ferric salt rendered sufficiently basic gives a thin and brittle leather ; and (3) the ferric salt in such a condition readily acts as a catalyst and brings about harmful oxidations in the leather. In his own experiments, in which four liquors were tried, Casaburi obtained the best results with a basic ferric sulphate liquor obtained by acidifying a ferrous sulphate solution and then completely oxidising with nitric acid. After tanning in this liquor the leather was well washed in water and steeped for 2 hours in a solution of sodium sulphate at

[11] Eng. Pat. 120298 ; *J.*, 1919, 189A.
[12] *Chem.-Zeit.*, 1919, **43**, 318 ; *J.*, 1919, 547A.
[13] *Chim. et Ind.*, 1919, **2**, 1024 ; *J.*, 1919, 917A.
[14] U.S. Pat. 1289250; *J.*, 1919, 189A.
[15] *J. Soc. Leather Trades' Chem.*, 1919, **3**, 61, 74 ; *J.*, 1919, 547A.

40° C. After a second thorough washing the leather was lightly oiled on the grain and dried Analysis showed the leather to contain 6·17% of ferric oxide and 68·3%, of hide substance Apparently the leather was of good quality though nothing very definite is said on this head, and it will be interesting to know how the leather keeps on storing, as permanent good quality has not been a feature of iron-tanned leathers so far

An interesting point in this experiment was that the iron liquor had the same basicity (*i.e.* ratio of iron to sulphuric acid) after use as when made up. Ferric chloride and ferric acetate liquors proved useless.

In vegetable tanning most of the developments have been in the mechanical side of the process, and aim at increased speed of production through quickening the actual tanning and diminishing the handling of goods. F. Gilardini [16] patents a process by which tan liquor is forced through hide by high pressure ; tanning is complete in a few minutes. This process reminds one of Müntz and Ramspacher's [17] method of tannin analysis, in which the tanning infusion was detannised by exactly the same means. A. N. Walker [18] and G. Randall [19] have patented devices for causing circulation of tan liquors in pits by means of compressed air. The former of these has already been described under liming. The latter process involves suspension of the hides from a frame over the pit, and the compressed air is introduced by perforated pipes along the bottom of the pit The liquors are thus kept in motion and insoluble matter does not settle out. R. Kay [20] has patented a means of circulating liquors through a series of pits, whether for liming or tanning. S. Saxe [21] patents the use of osage orange wood extract for drum tanning after hides have been partly tanned in weak vegetable liquors. This is a comparatively new material, showing a high content of tannin by the ordinary method of analysis and apparently closely related to fustic. It has a very decided effect in brightening the colour of vegetable-tanned leather, particularly when mangrove or quebracho has been used, and is of course quite harmless, which cannot be said of some methods for brightening colour.

Sulphite-cellulose or " spruce extract " is not a new material, but is coming now into greater prominence as better products are becoming available, principally from America. Whilst it cannot of course be used alone, there is no doubt that excellent leather can be made by using quite considerable quantities in conjunction with other materials provided that the sulphite cellulose be of good quality.

[16] Eng. Pat. 114631 ; *J* , 1919, 297A.
[17] *Comptes rend.*, **79**, 300 ; *Leather Ind. Lab. Book*, 173.
[18] Eng. Pat. 124992 ; *J.*, 1919, 331A
[19] Eng. Pat. 133823 : *J.*. 1919, 918A. '
[20] Eng. Pat. 128339 ; *J.*, 1919, 649A.
[21] U.S. Pat. 1297255 ; *J.*, 1919, 431A.

All tanners who have the nitrogen content of their leather systematically determined during progress through the tanyards are aware that tanning is much more rapid in the early stages than later. New experiments by A. Rogers [22] and O. Riethof [23] fully bear this out and show that half the total absorption of tannin is effected in the first 15-30 days. When the hides are halfway through in respect of time they are about four-fifths tanned. It is obviously a serious error to assume, as is often done in costing, that the goods are on the average half tanned.

A most interesting paper by C. F. Cross, C. V. Greenwood, and M. C. Lamb [24] deals with the principle of restrained tannage, a principle substantially incorporated in Turnbull and Carmichael's patent, noticed in last year's Report, for tanning in starch solutions. A colloid is used which has affinity for the tannin, but which will part with it to the hide. Thus, if strong liquors containing such a colloid are presented to the hide, there is no rapid over-tanning of the surface causing case-hardening and preventing penetration. Although the immediate surface will be more slowly tanned than in the absence of the colloid, because the hide can only take up tannin as the colloid releases it, yet complete tanning is very rapid as there is no obstacle to penetration. Various methods of applying this principle are described. One is to drum the hides for 2-3 hours in strong gum-tragasol jelly, until they are thoroughly impregnated, and then to treat them with strong tanning extract. In this case the reaction takes place in the hide, and the interstices of the leather are filled with the tannin-tragasol compound. The final product has a smoother texture, greater weight, higher resistance to water, and brighter colour than when tanned without tragasol. The colloid may also be similarly employed with equal advantage in chrome tanning. To the writer the principle appears to offer great promise of wide practical utility, and merits the careful attention of the tanner. Though it appears to offer the greatest advantage in the tanning of heavy leather, it will also be of importance in light leather manufacture, even though rapid methods are already in use.

A patent of importance is that of O. Röhm [25] for a new alum, salt, and flour tannage. Instead of the usual egg-yolk Röhm uses a sulphonated oil, from which the soaps have been removed for the most part, and dissolves it in a volatile solvent. The sulphonated oil has, like the egg-yolk, emulsifying and lubricating properties, and its price is very much lower.

[22] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 520 ; *J.*, 1919, 153A.
[23] *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 20.
[24] *J. Soc. Dyers and Col.*, 1919, **35**, 62 ; *J.*, 1919, 264A.
[25] Ger. Pat. 308386 : *J.*, 1919, 189A.

Other patents of less interest include that of L. Mauerhofer [26] who treats leather in a fulling mill with gelatin solution and nitric acid, in order to replace hide substance lost in earlier processes. Probably the protein-coagulating power of nitric acid is here brought into play. E. T. Dovan [27] treats leather with lead acetate and barium acetate in acetic acid solution The purpose of the treatment is to give hardness and water-resisting properties to the leather. It is difficult to see in these two patents the application of any useful principle.

Two patents have been granted for the preparation of basic chrome liquors. J. R. Blockey [28] patents the reduction of hexavalent chromium compounds by means of acid and waste organic matter, e.g., spent tan, waste leather, bark dust, etc. This method cannot have been in print before, but was certainly well-known to the writer and many others as it has been regularly given in lectures at Leeds for many years past, and can be seen in students' note-books. The same may be said of E Meyzonnier's [29] process in which bichromates are reduced by sodium sulphite and acid, and then rendered basic by means of further additions of sulphate. Indeed it is hard to name a reducing agent in ordinary use that will not produce a usable chrome liquor The following list is no doubt incomplete : Sulphites, bisulphites, sulphurous acid ; sulphides, hydrosulphides, hydrogen sulphide ; thiosulphates ; nitrites ; arsenious acid ; hydrogen peroxide ; stannous chloride ; ferrous sulphate ; all cellulosic materials, e.g , sawdust, shavings, spent bark, etc.: carbohydrates, e g , sugars, starches ; proteins : most other easily oxidisable organic substances, e.g., alcohols and fats. In a process patented by C. Blanc,[30] chromic acid is reduced by sawdust, or cotton and paper waste, or any cellulosic material.

M. C. Lamb [31] patents a process for the important purpose of stripping, i.e., de-tanning, chrome leather, in order that the hide substance may be utilised for glue manufacture. The disintegrated leather is washed and dried, and treated for 18 hours with a 15-40% solution of organic acids containing two or more hydroxyl groups, the best acid being oxalic. Chromic hydroxide may be precipitated from the solution, and the hide is washed in weak alkali and given the usual liming for glue making. The method is stated to give excellent results, and under favourable circumstances to yield hide suitable for the manufacture of gelatin. A. Wolff [32] for the same purpose uses a much more drastic procedure. The chrome leather waste is dissolved

[26] Eng. Pat. 118120 ; J., 1919, 836A.
[27] Eng. Pat. 126938 ; J., 1919, 591A.
[28] Eng. Pat. 131772 ; J., 1919, 783A.
[29] Eng. Pat. 123785 ; J., 1919, 431A.
[30] Eng. Pat. 120049 ; J., 1919, 83A
[31] Eng. Pat. 132864 ; J., 1919, 572A
[32] Ger. Pat. 310309 ; J., 1919, 331A.

at 80°-90° C. in at least its own weight of 5% sulphuric acid. **After all** separated fat is removed, chromic hydroxide is precipitated by lime. From the filtrate gelatin is then obtained, after removing the lime.

The manufacture of tanning extracts is a developing industry, which has been specially stimulated by the disappearance during the war of many continental extracts. It may be stated that in several parts of the Empire, e.g., India, South Africa, and Australia, efforts are being made to build up an extract industry, and men competent to undertake such work are in great demand. Barks, etc., are not only more thoroughly exhausted in extract factories than in tanneries, but much is saved in shipping and freight charges, and spent wood can be more advantageously utilised. Certain materials that otherwise could not be profitably used on account of low tannin content can be utilised for extract manufacture. An interesting patent dealing with extract manufacture is that of R. Silberberger,[33] who finds that if pine bark is first extracted with a resin solvent such as benzine with a boiling point of 100° C. or slightly above, the subsequent yield of tannin on extraction with water is increased by 1·5%. Smaic and Wladika[34] describe a method of preparing solid extracts from comparatively weak liquors. The process is one that was originally used for milk evaporation. The cold liquor of strength 8·6° B. is atomised in a cold chamber from which the water vapour is continually and rapidly removed by suction. The extract settles in powdered form on the floor. By this process there is very little opportunity for changes to take place in the properties of the tannin such as darkening or insolubilisation, which occur at comparatively low temperatures if there is long exposure. An extract prepared by this method preserved exactly its original colour and composition as found by analysis, and the moisture was as low as 7·6%. C. T. Galey and O. Riethof[35] show very clearly that the sugar content of tanning extracts increases when higher extraction temperatures are used. An extract prepared at 143° C. in autoclaves contained four times as much sugar as one prepared at 99° C., and over twice as much per unit of tannin. This is probably due to the breaking up of cellulosic constituents of the wood. Commercial extracts made in autoclaves always contain more sugar than those made in open leaches.

A new type of fat liquor is described by O. Röhm,[36] in which the emulsifying agent is not soap or sulphonated oil, but finely-divided colloidal clay. If oil or fat is ground up with the clay it will then readily mix with water without any separation, and can be directly used as a fat liquor for the lubrication of the leather fibres. This is an interesting and important application of comparatively recent scientific work on oil emulsions.

[33] Eng. Pat. 130010; *J.*, 1919, 689A.   [34] *Gerber*, 1919, **45**, 189.
[35] *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 470; *J.*, 1919, 430A.
[36] Ger. Pat. 313803; *J.*, 1919, 955A.

ANALYSIS.

Tannin Analysis.

J. A. Wilson follows up a previous paper [37] on the influence of electrolytes on the determination of non-tannins by showing how the presence of calcium sulphate may completely upset a tannin analysis. This substance was chosen on account of its frequent occurrence in tannery waters, though its influence is complex, increasing the amount of insoluble matter as well as of non-tannins. In the first place a 0·05% solution of calcium sulphate was analysed for non-tannins and showed 117% of the total calcium sulphate present, proving that the hide powder had had the effect of concentrating the external solution. Two solutions of 11·3 grms. of quebracho extract were made up for analysis, one with distilled water, the other with 0·05% calcium sulphate solution. The figures for the two analyses in the above order were : total solids, 18·31, 52·44% ; soluble matter, 47·23, 49·91% ; insoluble, 1·11, 2·50% ; non-tannins, 11·00, 14·42% ; tannins, 36·23, 35·52% ; i.e., a loss of tannin of 0·71%. Calculation from the result with the simple calcium sulphate solution led to the expectation of a loss of 0·75% tannin. It seems obvious that tannin analysis cannot be put on a footing even empirically sound until some way is devised of allowing for the presence of electrolytes. Results by the present method in the case of certain synthetic tannins containing a high percentage of sodium sulphate must be very far from the truth. When Wilson's two filtered solutions were analysed by the Löwenthal method, i.e. titration with permanganate solution, the tannin found was 33·3 and 28·6%. The two solutions analysed in the same way before filtration proved to have each the same tannin content.

An oxidation method for tannin analysis is described by F. T. Lee, [38] who modifies Jean's method by using iodine in the same way as permanganate is used in the Löwenthal method. The Löwenthal factors are used, and the method gives results quite good enough for tannery control, for which it is intended.

G. Baldracco [39] wishes the present official gravimetric method to be modified with respect to the method of chroming hide powder for use in detannising. The method now used he regards as too troublesome. His proposal is to use a powder lightly chromed in manufacture and to wash it with a quantity of the tannin solution, after which a further quantity of solution is detannised by the wet powder. Baldracco claims that it gives results in complete accordance with the official method, and that it is much less troublesome, but this is contested by

[37] Ann. Repts., 1918. 3, 332 ; J., 1919, 152A.
[38] J. Soc. Leather Trades' Chem., 1919, 3, 8.
[39] J. Soc. Leather Trades' Chem., 1919, 3, 110, 197.

J. G. Parker,[40] who has cårried out analyses with Baldracco's own powder. A great difficulty with lightly-chromed hide powder is that its absorptive properties alter on long keeping. This defect has pre vented its adoption in the past, and, so far no remedy has been devised There is little doubt, however, that advances in knowledge since 190? have been so considerable as to render it advisable to re-open the whole question of quantitative tannin analysis, and many workers are anxious that this should be done. Whilst the principle of reckoning as tannin all that is absorbed by'hide powder under standard conditions is much the soundest that has yet been put forward, considering the object of the analysis, there are several important details in which improvement could be effected. Amongst several suggested by Prof Procter to the writer are the following : (1) acidity of liquors, which has so far been ignored, though it may easily outweigh the already regulated acidity of the hide powder, and which must in the light of modern colloid chemistry exert a marked influence on absorption ; (2) the question of insoluble matter, much of which as at present esti mated is capable of tanning ; and (3) colour measurement, the present method not allowing a calculation for a solution of another strength. The, difficulty with electrolytes has been already mentioned.

R. H. Wisdom and W. A. Felder [41] find that unchromed hide powder gives results comparing favourably with those obtained with chromed powder if a slightly more acid liquor be used and the time of shaking be increased. Other workers [42] point out the importance of having kaolin free from acid-soluble matter when it is to be used with tannin solutions. It is not sufficient that it should be free from water-soluble impurities.

In the difficult region of qualitative tannin analysis there have been several papers published. R. Lauffmann [43] has studied the pine-shaving phloroglucinol reaction and finds that it gives roughly the usual separation into catechol and pyrogallol tannins, the test being generally positive with the former, and negative with the latter class. The same author [44] has substituted furfural for formaldehyde in the usual condensation test, and obtains brown precipitates which give on weighing " furfural precipitation numbers " closely agreeing with the corresponding formaldehyde numbers. If to the filtrate from these precipitates iron alum solution and, solid sodium acetate be added, a bright green zone is obtained with catechol tannins and a violet zone with pyrogallol tannins. C. M. Kernahan [45] in submitting a report

[40] *J. Soc. Leather Trades' Chem.*, 1919, **3**, 199.

[41] *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 239 ; *J.*, 1919, 472A.

[42] R. W. Frey, *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 393 ; *J.*, 1919, 473A D. McCandlish and F. B. Lederer, *ibid.*, 1918, **13**, 570 ; *J.*, 1919, 152A.

[43] *Ledertechn. Rundsch.*, 1919, **11**, 61 ; *J.*, 1919, 955A.

[44] *ibid.*, 1918, **10**, 97 ; *J.*, 1919, 379A.

[45] *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 512 ; *J.*, 1919, 835A.

of a Committee, states that sulphite-cellulose cannot be distinguished
from synthetic tannins by either the cinchonine or the p-nitraniline test,
and that if a material gives a positive Procter-Hirst test (i.e. with aniline
and hydrochloric acid) for sulphite-cellulose the best verification is a
high non-tannin content, as that of syntans is low. This the writer
doubts, as he has handled syntans containing 25% of non-tans, and a
further complication is that the Procter-Hirst test may be positive
with sulphited extracts having a low non-tannin content.

Leather Analysis.

A number of papers on leather analysis have appeared during 1919
of which perhaps the most important is the report of the committee of
the American Leather Chemists' Association on the extraction from
leather of oils and fats.[46] It appears to be proved that oxidised and
sulphonated oils are not completely extracted from leather by petroleum
spirit, and that chloroform is a much better solvent. An experiment
in which leather was extracted before and after fat-liquoring showed
that chloroform extracted a much greater excess in the second case
than did petroleum spirit. An objection was raised that chloroform
dissolved chrome soap, but it was found that this was equally the case
with petroleum spirit. It is suggested, however, that it may be advis-
able to have another solvent for sole leather, as chloroform appears to
extract some of the excess tannin, and on evaporation leaves a very
dark residue. The superior efficiency of chloroform, however, for fat
extraction is clearly proved and it is verified by F. P. Veitch and M.
G. Hunt,[47] who have experimented with mixtures of sand and known
amounts of fat. Petroleum spirit is only satisfactory for paraffins and
petrolatum.

The determination of water-soluble matter is dealt with by R.
W. Frey and I. D. Clarke[48] and by H. C. Reed and J. B. Churchill.[49]
The former authors show conclusively the insufficiency of 3 hours'
extraction even when, as in the United States, two litres of water is
used. Taking as 100% the amount extracted in $7\frac{1}{2}$ hours, the amounts
removed in shorter periods are as follows : in 3 hours 85–90%,
$4\frac{1}{2}$ hours 92–94%, in 6 hours 96·7–97·4%. Probably not more than
80% is extracted in 3 hours with one litre of water. The same authors
also find about 0·9% increase in water-soluble matter for 5° C. increase
in extraction temperature between 45° and 55° C. Reed and Churchill
describe an ingenious apparatus for automatic extraction which gives
excellent results.

[46] J. Amer. Leather Chem. Assoc., 1919, 14, 140 ; J., 1919, 380A.
[47] ibid., 1919, 14, 507 ; J., 1919, 835A.
[48] ibid., 1919, 14, 488 ; J., 1919, 836A.
[49] ibid., 1919, 14, 133 ; J., 1919, 380A.

The important determination of free mineral acid in leather has again been worked on by a Committee [50] and a slightly modified form of the Procter-Searle method is recommended. Care should be taken to treat the leather with a considerable excess of sodium carbonate solution, and after evaporation and ignition the ash is digested for some time with the equivalent amount of sulphuric acid before titrating with carbonate for excess acid. R. F. Innes [51] has shown that the small amount of sulphur present in many chrome leathers is completely extracted by petroleum spirit, and that a further extraction with carbon bisulphide is superfluous. A. Harvey [52] determines the moisture content of leather by distilling with dry petrol of b. pt. 150°–200° C. and measuring the water carried over. Results obtained in half-an-hour agree almost exactly with those given by drying for 4 hours *in vacuo* at 100° C.

Semo leather analyses by E Seel, K. Hils, and K. Reihling [53] reveal how widespread was the use of synthetic tanning materials in Germany during the war. Amongst very many samples analysed, only three gave negative tests for synthetic tannins.

The effect of grease on the tensile strength of harness leather has been studied by L. M. Whitmore, R. W. Hart, and A. J. Beck, [54] who find that about 14% of grease increases the tensile strength of leather by 14-20%. Further additions of grease have no effect. They ascribe this effect to the lubrication of the fibres, which allows a little slipping, producing a greater elongation and better distribution of the strain. Probably the fibres themselves are strengthened. A degreased leather gives a sharp break, very different from the frayed edges given by well-stuffed material.

Chrome Leather, etc.

The study of the analysis of chrome leathers has been undertaken by a Committee of the Society of Leather Trades' Chemists. The first results published [55] show that fusion of chromic oxide or chrome leather ash with sodium carbonate and potassium chlorate to convert into chromate, works very satisfactorily, without requiring platinum crucibles, as also does fusion in nickel crucibles with sodium peroxide. K. Schorlemmer [56] finds that in oxidising chromic salts with hydrogen peroxide in alkaline solution, a little ferric chloride facilitates the reaction and overcomes the inhibiting effect of organic matter (*e.g.*

[50] *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 330.

[51] *J. Soc. Leather Trades' Chem.*, 1919, **3**, 126; *J.*, 1919, 955A.

[52] *ibid.*, 1919, **3**, 128; *J.*, 1919, 955A.

[53] *Z. angew. Chem.*, 1919, **32**, 4; *J.*, 1919, 431A.

[54] *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 128; *J.*, 1919, 380A.

[55] *J. Soc. Leather Trades' Chem.*, 1919, **3**, 194.

[56] *Collegium*, 1919, 5; *J.*, 1919, 815A.

protein) when present in small quantities. Larger quantities of organic matter must be removed by evaporation and ignition, or by oxidising with permanganate.

Miscellaneous.

H. G. Bennett [57] gives an exact method of determining sulphides at great dilution. The solution is distilled with magnesium chloride in an atmosphere of carbon dioxide as in Feld's method, and the hydrogen sulphide is collected in $N/10$ iodine solution. The residual iodine is titrated by sodium arsenite solution. Not more than 10 mgms. of hydrogen sulphide must be collected for every 25 c.c of iodine solution, otherwise results are rendered inaccurate. Another paper by Bennett and N. L. Holmes [58] on the determination of nitrogen in gelatin by Kjeldahl's method confirms Sorensen's statement that prolonged digestion involves a gradual loss of ammonia.

THEORY OF TANNING, ETC.

Chemistry of Vegetable Tannins.

By far the most important advance here is the synthesis of gallotannic acid (the tannin of oak galls) by E. Fischer.[59] The study of the hydrolytic products of this substance showed that one molecule of glucose was combined with a number of molecules of gallic acid, probably ten, and that the constitution of gallotannic acid was that of a pentadigalloylglucose. The older work left great doubt as to whether glucose was a part of the tannin molecule, or only an associated impurity, and the view of most chemists was that gallotannic acid was m-digallic acid, as suggested by Schiff. This constitution, however, did not account for the optical activity exhibited by gallotannic acid, and the definite assumption that no glucose was contained in the molecule was always doubtful. Fischer,[60] assuming no free carboxyl groups to be present in the tannin molecule, adopted Perkin and Stiasny's method of purification by neutralising all free gallic acid present as impurity with weak alkali, and extracting the tannin with a solvent. The material thus purified gave regular results on hydrolysis and the value of the products was definitely established. The synthesis of tannin was then attempted step by step. Tricarbomethoxygalloyl chloride was prepared (the carbomethoxy groups protecting the hydroxy groups of the gallic acid from the action of the phosphorus pentachloride) and five mols. condensed with one mol. of glucose in the presence of quinoline, the carbomethoxy groups of the condensation

[57] J. Soc. Leather Trades' Chem., 1919, **3**, 190.
[58] J. Soc. Leather Trades' Chem., 1919, **3**, 24.
[59] Ber., 1918, **51**, 1760; 1919, **52**, 829; J., 1919, 47A, 429A.
[60] Ber., 1912, 915, and 1913, 1116.

product being afterwards removed by cold alkali. The final product, pentagalloylgluçose, was remarkably like gallotannic acid, being astringent, optically active, and faintly acid; it precipitated gelatin and alkaloids. In attempting the synthesis of penta-*m*-digalloyl-glucose, difficulties were experienced in the preparation of the *m*-digallic acid and its acid chloride. Pentamethyl-*m*-digalloyl chloride, however, was prepared and condensed with glucose, and a product obtained penta(pentamethyl-*m*-digalloyl)glucose—which appeared to be identical with methylotannin obtained by methylating gallotannic acid. *m*-Digallic acid itself, however, did not yield a well-characterised carbomethoxy derivative or carbomethoxy acid chloride, and the attempt to condense the latter with glucose was indecisive. Recently, however,[61] crystalline pentaacetyl-*m*-digalloyl chloride has been prepared and this condenses easily with β-glucose yielding penta(penta-acetyl-*m*-digalloyl)glucose which when de-acetylated with sodium acetate gives penta-*m*-digalloyl-β-glucose. This substance is beyond all reasonable doubt an isomer of natural tannin, the difference between it and Chinese tannin being in the specific rotation in aqueous solution. The rotations in organic media show no difference from those obtained with Chinese tannin. In the latest paper on the subject[62] a method is given for preparing the pentadigalloylglucose in purer condition than before, and a series of acylglucoses is described very many of which (*e.g.*, trigalloylglucose) behave as tannins. The mono-acylglucoses do not precipitate gelatin, however. Trigalloylglycerol and hexagalloyl-mannitol yield colloidal solutions with water and precipitate gelatin.

Incidentally Fischer[63] has proved that the glucogallin isolated by Gilson from Chinese rhubarb is 1-galloyl-β-glucose.

K. Freudenberg, who has been associated with Fischer in much of the work on tannin, has investigated hamameli tannin and chebulinic acid. Hamameli tannin, which has been isolated in the crystalline condition, occurs in the bark of *Hamamelis virginiana*, a small tree common in North America, and is extracted by a mixture of ether and alcohol, after plant wax has been removed by petroleum spirit. Freudenberg[64] shows that on hydrolysis with tannase the tannin yields gallic acid and a sugar (apparently a hexose) in the proportions required for a digalloylhexose. Chebulinic acid, which appears in commerce as eutannin, occurs in myrobalans, the fruit of *Terminalia chebula*, and crystallises in rhombic prisms, sparingly soluble in cold water. Freudenberg[65] shows that it probably contains a free carboxyl group and that it cannot be hydrolysed by tannase. It appears to be a compound

[61] *Ber.*, 1918, 51, 45.   [62] *Ber.*, 1919, 52, 829; *J.*, 1919, 429A.
[63] *Ber.*, 1918, 51, 1760; *J.*, 1919, 47A.
[64] *Ber.*, 1919, 52, 177; *J.*, 1919, 296A.
[65] *Ber.*, 1919, 52, 1238; *J.*, 1919, 591A.

of a crystalline tannin, apparently a digalloylglucose, and a new phenolic acid, the latter attached to the glucose to form a glucoside.

Since Fischer undertook the investigation of tannins the progress made has rendered obsolete the greater part of the work of a century, and his recent death is the greatest possible misfortune in this, as in other fields of organic chemistry.

Collagen and Gelatin.

A Ewald [66] has studied the shortening of collagen fibrils on heating in water, which is very remarkable in the case of fibres previously purified by tryptic digestion. The behaviour of collagen after treatment with formaldehyde is so characteristic that it may serve as a new qualitative test. At 93° C. the fibres shrink to one-third of their original length and extend to two-thirds their length on placing in cold water. When treated again at 69° C. they again contract to one-third but regain their origina; length completely on keeping for some time in cold water. The collagen used was from the tendon of the mouse. Gelatin is still being worked on from the biochemical standpoint, particularly in America. J. Loeb has published several papers [67] on the chemical behaviour of gelatin, supporting his views that gelatin is practically undissociated at its iso-electric point, and that on the alkaline side of this point it can combine only with kations, whilst on the acid side it can combine only with anions. This Loeb has verified by the analysis of iron-protein compounds. All such properties as swelling, osmotic pressure, and viscosity, in the presence of electrolytes, show very distinct minima at the iso-electric point (p_H 4·7). The details of Loeb's work cannot be entered into here but its significance is very great, showing the prime importance of an exact knowledge of hydrion concentrations before attempting to interpret any results obtained in the investigation of gelatin.

The imbibition of water by gelatin has been shown by E. B. Shreve [68] to increase with rise of temperature. According to Le Chatelier's theory, since the absorption of water by gelatin is accompanied by the evolution of heat and contraction, it should be favoured by cold and by pressure. The author suggests that there is no contradiction here but that the rate of absorption is so low as to prevent the attainment of equilibrium and the higher results with increase of temperature are due to higher rates of imbibition. C. R. Smith [69] from a study of the mutarotation of gelatin solutions inclines to the view that there are two forms of gelatin—the sol form A, stable above 33°-35° C.,

[66] Z. physiol. Chem., 1919, 105, 115, 135; J., 1919, 591A.
[67] J. Gen. Physiol., 1918, 1, 237; 1919. 1, 363. 483; J., 1919, 331A.
[68] J. Franklin Inst., 1919, 187, 319; J., 1919, 296A.
[69] J. Amer. Chem. Soc., 1919, 41, 135; J., 1919, 228A.

and the gel form B, stable below 15° C. At intermediate temperatures the two forms co-exist and mutarotation is due to the transformation of one into the other by a reaction reversible with temperature and apparently bimolecular. Increase in lævorotation, indicating increasing formation of the gel form B, follows closely increase in viscosity. F. C. Thompson [70] has reviewed the evidence for the network structure of gelatin jellies and solutions, and advocates the view that a gelatin solution which is too dilute to set, is nevertheless, at a concentration above 0·2%, an elastic solid. It is interesting to note in this connection a paper by E. A. and H. T. Graham,[71] who find that the diffusion of acids into gelatin jellies is very distinctly retarded by the presence of sugars in the jelly, though they are unable to give what they consider a satisfactory explanation. Accepting the view above mentioned that a gelatin jelly is a network of solid gelatin with interstices of molecular dimensions, containing the liquid from which the jelly has been made, it is easy to see that the diffusion of electrolytes must be retarded when sugar is present, as this substance raises the viscosity of water and thus retards diffusion.

The work of Tolman and Stearn on the swelling of fibrin in acid solutions has been followed by a study of swelling in alkalis.[72] The original theory of swelling [73] is adopted as the results are held to confirm it. With strong alkalis a maximum swelling was attained at concentrations below 0·05N. With ammonia swelling increased gradually up to a concentration of 0·8N. R. S. Bracewell [74] maintains that the amount of acid neutralised by the proteins is determined by the number of free amino groups in the molecule, which is in disagreement with Robertson's view, which is that the free amino groups in proteins are insufficient in quantity to account for the neutralisation. Bracewell, however, points out that free amino groups may exist which do not react with nitrous acid and it is on the nitrous acid reaction that Robertson bases his opinion.

Basic Chrome Liquors.

In continuation of the work referred to in last year's Report, there is a paper by M. E. Baldwin [75] in which the action of neutral chlorides on chromium chloride liquors and on hydrochloric acid is investigated. It is well known that sodium chloride stabilises basic chrome liquors. *i.e.* causes a requirement of more alkali to start precipitation -in other

[70] *J. Soc. Leather Trades Chem.*, 1919, **3**, 209.

[71] *J. Amer. Chem. Soc.*, 1918, **40**, 1900.

[72] R. C. Tolman and R. S. Bracewell, *J. Amer. Chem. Soc.*, 1919, **41**, 1503; *J.*, 1919, 918A.

[73] *Ann. Repts.*, 1918, **3**, 338.

[74] *J. Amer. Chem. Soc.*, 1919, **41**, 1511; *J.*, 1919, 918A.

[75] *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 10.

words, the liquors then behave as though more acid, and the author's object was to see if this could be confirmed by measurements of hydrogen ion concentration. Solutions of chromic chloride were prepared containing 13·77 grms. per litre of chromic oxide, and to these solutions 1, 2, 3, 4 grm.-molecules of sodium chloride were added per litre. The concentration of hydrogen-ions rose from 0·006 in the case of the simple chrome liquor to 0·025 when 4 grm:-molecules of sodium chloride were added per litre. The effect of barium chloride was even more marked. The order of effect is : KCl NH₄Cl NaCl LiCl BaCl₂ : this order corresponds with the order of degree of ionic hydration for these salts. The same effect of salts may be observed with hydrochloric acid instead of chromic chloride solution. The explanation offered is that the salts take up water for the hydration of their ions, thus leaving a less quantity for the solution of the acid. Thus a distinction should be drawn between concentration of hydrions per litre of solution and concentration of hydrions per litre of available solvent. J. W. McBain,[76] however, offers another explanation of this effect, in an investigation of acetic acid to which sodium chloride had been added He found that an increase in the hydrion concentration was paralleled by an increase in the vapour pressure of the undissociated acetic acid. This he regards as due to an enhanced chemical potential in the presence of such salts as sodium chloride, and he considers that there is no need to alter the dissociation constant of acetic acid. These two explanations are, perhaps, reconcilable.

Theory of Tanning.

W. Möller [77] has written on several aspects of the theory of tanning. In the case of oil tannage with mixtures of fish oils and phenols he regards his peptisation theory as borne out, the phenols acting as peptising agents. The oxidised fish oil itself has tanning properties. Oleic and stearic acids also tan in presence of phenols, but the leathers do not much resemble chamois leather. Mixtures of phenols with mineral oil have also tanning action on pelt, and thus the presence of active groups (for example hydroxyl and carboxyl groups) is not essential.

In currying and fat-liquoring [78] the unsaturated fatty acids in fish oils are oxidised to peroxides which with water split up into dihydroxy-acids and an atom of oxygen, which active oxygen oxidises the polyphenols present in vegetable tannins forming insoluble substances like the phlobaphenes. These insoluble substances greatly increase the waterproofness of leather and diminish the amount of water-soluble matter. On the physical side the action of currying and fat-liquoring

[76] *Chem. Soc. Trans.*, 1919, **115**, 1332.
[77] *Collegium*, 1919, 61, 72 ; *J.*, 1919, 783A.
[78] *Gerber*, 1919, **45**, 277 ; *J.*, 1919, 917A.

is attributed to the formation of emulsions. Tawing is regarded not as a tannage but simply as a colloid-chemical impregnation of the skin with fat.

GLUE.

A method of separation of glue and similar substances in vegetable glues is given by W. Donselt.[79] The substance is boiled for several hours with water only, and then for a short time with the addition of tartaric acid. After nearly neutralising' with alkali, albuminous matter is precipitated by saturated zinc sulphate solution, and the solution made up to a definite volume. The nitrogen in the filtrate and precipitate is determined by Kjeldahl's method. An aliquot part of the filtrate is precipitated with tannin and acetic acid solution and the nitrogen again determined in the filtrate. This last value subtracted from that obtained before precipitation with tannin gives the nitrogen corresponding to the original glue content. F. L. Browne[80] describes water-resistant glues. Gelatin glues can only be made resistant by waterproof coatings, which it is not always practicable to apply. Blood albumin and casein glues are more resistant in themselves to water. Although there is some absorption, the saturated glue has still considerable strength. Details are given for the preparation of such glues.

Patents describing the stripping of chrome leather for glue manufacture have been mentioned on p. 353 ; of other patents, two may be referred to. R. W. Mumford[81] describes the clarifying of glue by the use of porous vegetable carbon of open texture possessing nearly the same cellular structure as the material from which it was made. J. Alexander[82] prepares glues soluble in cold water, by first mixing the glue with a substance such as calcium chloride which evolves heat on solution in water.

[79] *Z. Spiritusind.*, 1919. **42**, 44 ; *J.*, 1919. 547A.
[80] *Chem. and Met. Eng.*, 1919, **21**, 136 ; *J.*, 1919, 732A.
[81] U.S. Pat. 1289053 ; *J.*, 1919. 153A.
[82] U.S. Pats. 1300096 and 1300097   *J.*, 1919, 473A.

AGRICULTURAL CHEMISTRY.

BY E. J. RUSSELL, F.R.S ,

Director of the Rothamsted Experimental Station.

So far as the output of papers is concerned, 1919 is one of the lean years of agricultural chemistry. Three causes have operated : the staffs of the Experiment Stations are only now returning to agricultural research problems after their special work during the war ; the colleges have been overflowing with students so that teachers have had neither time nor opportunity for doing research ; and no supplies of experienced post-graduate workers are yet forthcoming. These causes have operated throughout the civilised world, even America being affected ; fortunately they are only temporary and are even now in course of removal.

There are several distinctly promising signs for the future. The Board of Agriculture has prepared a scheme which, if sanctioned by the Treasury, will provide considerable funds for improving the status of the research worker. Another very hopeful sign is the establishment by the Olympia Agricultural Co. of a large research department to occupy itself with agricultural investigations. Professor C. Crowther of the University of Leeds has undertaken the direction of the work, and he has already been able to secure the services of two of the best of the younger men, Mr. C. T. Gimingham of the Long Ashton Fruit and Cider Institute, and Mr. H. Hunter of the Irish Department of Agriculture.

The papers published during the year have dealt in part with the aftermath of war problems and in part with problems of the future.

FERTILISERS.

Among the most important information desired by the fertiliser manufacturers is the probable consumption of artificial fertilisers by farmers in the United Kingdom during the next ten years. A Departmental Committee attempted during the war to arrive at a good estimate and their full report is now published [1] containing the figures and passages omitted from the Report issued previously. The estimates contained therein are high, and perhaps may not be easily reached. Yet the consumption is increasing considerably. In view of the im-

[1] *Cd.* 8994, 1918.

portance of the figures and their general inaccessibility they are brought
together here ; they relate to the United Kingdom and are given in tons.

	Pre-war consumption.	Actual consumption, year ending May 31.		Estimate in Post-war and Sulphuric Acid Report.	
		1918.	1919	Sir T. H. Middleton	Sir Chas. Fielding.
Sulphate of ammonia	60,000	234,000	269,000	}	} 360,000
Nitrate of soda . .	80,000*	practically none used			
Superphosphate . .	743,000	720,000	750,000	1,367,000	1,643,000
Basic slag	263,000	500,000	540,000	892,000	1,463,000
Potash salts . . .	100,000	10,000	- -	- -	—

* In addition about 10,000 tons of nitrolim and nitrate of lime were used.

It is possible that the 360,000 tons of nitrogenous manures in Sir
Charles Fielding's estimate is on the low side and that another 100,000
tons might profitably be used.   However this may be, there is no lack of
scope for the fertiliser manufacturer, and given good quality in fertilis-
ers, intelligent propaganda, and adequate salesmanship, there should
be no difficulty in maintaining a good demand.

The Alkali Inspector reports considerable activity among chemical
manure manufacturers ; the number of registered works and the power
of production have increased, the adoption of mechanical dens in super-
phosphate works has extended, and new types of appliances have been
introduced.[2]

There was a general expectation of cheap fertilisers and of over-
production at the end of the war, a fear which clearly dominated the
Post-War and Fertiliser Committee ; but nothing of the kind has hap-
pened.   German competition has been non-existent, in spite of their
favourable and rather bombastic anticipations.[3]   They claim to have
fixed 400,000 tons of nitrogen in 1916, and they had expected to be
able to export annually nitrogen compounds equivalent to 750,000 tons
of Chilean nitrate.[4]   Apparently they are not turning out a great deal,
and their own requirements are heavy : Neubauer estimates them
at 360,000 metric tons of combined nitrogen a year as against 100,000
tons before the war.[5]   So far from there having been any over-produc-
tion, complaints have arisen in Denmark,[6] Holland,[7] and Japan,[8] and

[1] *Alkali Inspector's Rept. for 1918 ; J., 1919, 315R.*
[2] *Z. angew. Chem., Mar. 21, 1919 ; J., 1919, 189R.*
[3] R. E. McConnell, *J. Ind. Eng. Chem.*, Sept., 1919.   [1] *J., 1919, 304R.*
[4] *Z. angew. Chem.*, Jan. 3, 1919 ; *J.*, 1919, 108R.
[5] *Ibid.*, Jan. 21 ; *J.*, 1919, 108R.
[6] *U.S. Com. Rept*, Apr. 8, 1919 ; *J.*, 1919, 208R.   600,000 tons of chemical
fertilisers are now used annually in Japan in addition to oil cake valued at £7,000,000
imported from Manchuria.

elsewhere that sufficient fertiliser cannot be obtained, and that consequently the countries which formerly imported must produce for themselves.

The search for raw materials continues unabated. Nitrates[9] are recorded in South Africa in crevices of some of the mountains : it is presumed they are formed by the nitrification of animal droppings, and owe their preservation to sheltering ledges of rock. It is not clear, however, that the supplies will be of more than local interest. Phosphates are recorded from N.E. Holland, containing 25 to 30% phosphate,[10] and from Saldanah Bay (South Africa) containing 14 to 16% P_2O_5 ; an out-turn of 2000 to 3000 tons per month from the factory is anticipated.[11] Other supplies are announced from Cape Cross for delivery at Capetown. Attention has also been directed to the Egyptian phosphates, which are claimed to resemble those of Algeria and Tunis, and have hitherto been sent to Japan or converted into tetraphosphate. In 1917, 115,732 tons had been worked : in 1918, only 31,147.[12] The most interesting development is that of Alsatian potash. Prior to the war, is as well known, almost the whole of the world's supply of potash was drawn from the Stassfurt mines in Germany, the Alsatian deposits remaining undeveloped. Now that Alsace is returned to France the Alsatian mines are to be worked ; a start has been made, and as long ago as last April, the daily output was 2500 metric tons of crude salts [13] ; it is expected shortly to become 4000 metric tons daily, and by 1922 is estimated at 9000 tons daily.[14] The deliveries for the first six months of 1919 were 131,531 metric tons of salts equivalent to 27,543 tons K_2O. In 1913 the total consumption in France had been only 35,000 tons K_2O.[15] An interesting account, written, however, for propaganda purposes, is given in the report by F. Binder.[16] Meanwhile the output of the Stassfurt mines is seriously falling off : it was barely 120,000 metric tons in the first three months of 1919, against 300,000 metric tons in the corresponding quarter of 1918.[17] Naturally there is some nervousness in Germany, although a bold front is maintained.

The world's consumption of potash before the war was about 14 million tons of potassium salts annually.[18] Assuming the Alsatian mines to develop as rapidly as is anticipated, it becomes doubtful to what extent the wartime potash supplies in this country will be able to withstand the competition. Rossiter and Dingley take a cheerful view of

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[9] G. E. B. Frood and A. L. Hall, *Union S. Afric. Dept. Mines and Ind. Geol. Survey Memoir*, 14, 1919 ; also E. G. Bryant, *J.*, 1919, 360T.

[10] *U.S. Com. Rept.*, May 12, 1919 ; *J.*, 1919, 292R.

[11] *J.*, 1919, 228R.   [12] *J.*, 1919, 187R.

[13] *J.*, 1919, 397R.   [14] *J.*, 1919, 231R.

[15] *Z. angew. Chem.*, Oct. 3, 1919 ; *J.*, 1919, 437R.

[16] *J.*, 1919, 218R.   [17] *J.*, 1919, 200R.

[18] *Z. angew. Chem.*, July 8, 1919 ; *J.*, 1919, 293R

the future, however, and estimate that the blast furnaces of England and Wales can produce 80,000 tons per annum of KCl, equivalent to 50,000 tons K_2O, which is double the pre-war consumption in the United Kingdom.[19]

The fertiliser trials with blast-furnace flue dust [20] showed distinct promise, but it is by no means clear that the effects were always due to the potash.[21]

In the United States the position is perhaps more secure, the total production during 1918 having been 192,587 tons.[22]   For the four years before the war the amount imported had been about a quarter of a million short tons per annum. America is therefore within sight of being self-supporting if she finds it worth while to be so.[23]   It is reported that American importers of foreign potash are compelled by law to purchase at the same time a corresponding amount of the home product.[24]

Of the manufactured fertilisers the nitrogenous compounds are of great interest in view of their high price and their obvious effect on growing crops. At the termination of hostilities there were large quantities of ammonium nitrate immediately available as fertiliser, and also of cordite, which becomes available after hydrolysis and conversion into calcium nitrate. It is understood, however, that stocks of cordite are no longer available, so that the question of agricultural utilisation has already passed into the category of closed war problems. But ammonium nitrate remains as a fertiliser of distinct promise [25] which would be worth some £10 per ton if sulphate of ammonia and nitrate of soda each cost £21 per ton.

Nitrate of lime has not yet appeared in English country markets though it also is a good fertiliser. A considerable amount of work has been done on calcium cyanamide, sold as fertiliser under the name of nitrolim. Hitherto it has come to us from the Continent, but a project is on foot to manufacture it in this country.[26]   This substance has been before farmers for some years, but during the war was used for other purposes : investigation has continued, however, and much knowledge has been gained. Prior to the war it was looked upon as rather uncertain in its effects ; it might do good or it might do harm. G. A. Cowie has made a valuable investigation [27] which clears up the apparent discrepancies. He shows that the decomposition of cyanamide in field soils proceeds in three stages : first of all urea is formed, then ammonia, then nitrate which is assimilated by the plant. In a

[19] E. C. Rossiter and C. S. Dingley, *J.*, 1919, 375T.
[20] *Ann. Repts.*, 1919, **3**, 352.
[21] *J. Bd. Agric.*, 1919, **26**, 387.   [22] *J.*, 1919, 374R.
[23] *U.S. Geol. Survey*; *J.*, 1918, 264R; 1919, 248R.   [24] *J.*, 1919, 293R
[25] E. J. Russell, *J. Bd. Agric.*, 1919, **25**, 1332 ; *J.*, 1919, 228A.
[26] For the proposed factory at Workington, see *J.*, 1919, 46R.
[27] *J. Agric. Sci.*, 1919, **9**, 113 ; *J.*, 1919, 380A.

normal good soil the changes take place quickly and the cyanamide has a high value as fertiliser. The first part of the change is brought about by purely chemical agency and is not bacterial ; the second and third, however, are brought about by means of micro organisms. The chemical agent necessary for the first stage is not present in all soils ; in its absence the cyanamide does not decompose and therefore fails to act as manure. Attempts are now being made to find the active agent and to design simple tests showing whether or not it is present in a given soil. Commercial nitrolim often contains the polymeric form dicyanodiamide which is toxic to plants and should therefore be avoided ; this involves a factory problem which ought not to be insoluble and which must be solved if the fertiliser is to receive sympathetic treatment at the hands of British experts.

These conclusions are confirmed by independent workers on the Continent. P. Mazé, Vila, and M. Lemoigne [28] in France, showed that cyanamide decomposes in culture solution to urea, which then changes to ammonium carbonate ; in this case, however, the formation of urea could be brought about by micro-organisms. In Germany also it has been shown [29] that the dicyanodiamide is harmful and must be avoided. Mazé and his colleagues have indeed claimed [30] that the dicyanodiamide is only inert and that the cyanamide is harmful until it is decomposed, but their experiments were made in water cultures and not in soil.

A new method of estimating dicyanodiamide in cyanamide has been suggested [31]

Cyanamide is largely used in practice in conjunction with superphosphate, and a method has been patented which allows of the simultaneous manufacture of the two fertilisers on the same works. Phosphate rock and calcium carbonate are heated to 1200° C. in producer gas, giving rise to lime and phosphorus, which volatilises and is oxidised to phosphoric anhydride ; the temperature is then raised to 1500° C. when calcium carbide and then cyanamide are formed.[32]

Little has been added to our knowledge of ammonium sulphate during the year. Further details of its toxic effect on barley in sand cultures devoid of lime are recorded by H. G. Söderbaum.[33] The possibility of using nitre cake in place of sulphuric acid has been discussed by Dawson,[34] and if the need arises again makers will be in a much better position than they were in 1917 when the problem was first presented to them. Methods of increasing the recovery have been

[28] Comptes rend., 1919, 169, 921 ; J., 1920, 36A.
[29] Hövermann and F. Koch, J. Landw., 1916, 64, 317 ; J., 1919, 837A.
[30] Comptes rend., 1919, 169, 804 ; J., 1919, 918A.
[31] F. W. von Dafert and R. Miklauz, Z. Landw. Vers.-Wesen Deutsösterr., 1919 22, 1 ; J., 1919, 837A.
[32] E. W. Haslup, U.S. Pat. 1281363 ; J., 1919, 12A.
[33] H. G. Söderbaum, Bied. Zentr., 1919, 48, 133 ; J., 1919, 507A.
[34] H. M. Dawson, J., 1919, 987.

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suggested,[35] but the details are of more interest to the gas or coke-oven chemist than to the agriculturist. An account is now published[36] of the German difficulties in making ammonium sulphate towards the end of the war which no doubt contributed to the dearth of nitrogenous fertilisers there.[37]

During the war there were persistent accounts that urea was to be used in Germany as a fertiliser and it has formed the subject of various patents.[38] Urea is shown to be at least equal to ammonium sulphate or sodium nitrate in its effects,[39] besides being more concentrated : its advantage lies apparently in the saving of transport. Other ammoniacal manures are described by C. Bosch.[40]

History repeats itself in agriculture as elsewhere ; recently patents[41] have been taken out by Swedish chemists for the bacterial production of nitrates the process used by Swedes in the great Thirty Years War of the seventeenth century.

Phosphatic Manures.

Years ago there was in this country a discussion as to whether rock phosphate needed treatment with sulphuric acid to convert it into a good fertiliser, and whether anything was required beyond admixture with ammonium sulphate. It was recognised that mineral phosphate alone was inferior to superphosphate alone, but it was claimed that the mixture of mineral phosphate + ammonium sulphate was fully equal to that of superphosphate + ammonium sulphate. The discussion was not taken seriously by experts at the time and it was soon forgotten. During the war the question was reopened owing to the shortage of sulphuric acid. But it took another form, that of determining whether the solubility of the phosphate should be increased by any other means than by acid treatment. Heating to a high temperature was found to have this effect, and several processes have been described.[42] In India it has been suggested that the cheap power available at the Tata Hydro-electric works might enable something similar to the Palmaer process to be used.[43] The original form of the problem has formed the

[35] F. Sommer, *Stahl u. Eisen*, 1919, **39**, 261 etc. ; *J.*, 1919, 350A. M. Heineken, *J. Gasbeleucht.*, 1919. **62**, 39 ; *J.*, 1919, 251A. *Times Eng. Suppl.*, Aug., 1919.

[36] " Food Conditions in Germany," *Cd.* 280, 1919.

[37] E. Wolff, *J. Gasbeleucht.*, 1918, **61**, 577 ; *J.*, 1919, 103A. A. Krämer, *ibid.*, 1919, **62**, 344 ; *J.*, 1919, 627A.

[38] *E. g.* Badische Anilin u. Soda Fabrik, Ger. Pat. 308659 ; *J.*, 1919, 48A.

[39] E. A. Mitscherlich, S. v. Saucken, and F. Iffland, *J. Landw.*, 1918, **66**, 187 ; *J.*, 1919, 153A.

[40] *Z. Elektrochem.*, 1918, **24**, 361 ; *J.*, 1919, 191A.

[41] C. T. Thorssell and H. L. R. Lunden, U.S. Pats. 1286838-9, and 1288754-6 ; *J.*, 1919, 134A.

[42] See *e.g.* U.S. Pat. 1281681 ; *J.*, 1919, 48A.

[43] *J.*, 1919, 228R.

subject of some discussion in America, and it has been argued [44] that a secondary effect of the SO_4 ion would be to dissolve the insoluble phosphate. J. Hendrick has contributed an interesting discussion [45] of the problem in which he maintains that the advantage of converting rock phosphate into superphosphate is not in all cases worth the cost, hence " it should be possible in future to use a large part of the rock phosphate in the form of finely-ground powder instead of in super-phosphate." These and other investigations have brought into prominence the question of the evaluation of mineral phosphates, and it is again shown that the proportion dissolved in citric and nitric acids depends on the conditions of the experiment, [46] and is not a definite constant.

The interaction between ammonium sulphate and superphosphate has been studied by Fowweather. [47] It is well known that mixtures of these two substances tend to set, and this change has a good deal to do with the development of the proper " condition " held to be necessary in a fertiliser. Before setting the mixture is moist and sometimes sticky ; after setting it becomes dry and is easily ground. The rate of setting is increased by addition of a little limestone to reduce the amount of free acid present.

The composition of manufactured superphosphate has been dis-cussed by Aita [48] in a long paper ; he considers that its physical pro-perties depend on the proportions of free phosphoric acid and of water : the former depending on the nature and physical condition of the com-ponents of the reaction, and the latter mainly on the concentration of the sulphuric acid used. In a good superphosphate (which he considers unusual) the free phosphoric acid should amount to less than 1% or 2%, and the dicalcium phosphate should be equivalent to the same amount : water should not exceed 10% or 12%. Many samples, however, are not so good ; they contain more than 12% of water, more than 2% of free phosphoric acid, and no dicalcium phosphate.

Several improvements in the apparatus for mixing or excavating in the manufacture of superphosphate are recorded. [49]

Basic slag has received a good deal of attention. The question whether solubility in citric acid is a proper criterion of value is still being discussed and evidence is forthcoming on both sides. F. Bain-bridge,[50] working at Skinningrove, shows that slag containing a high proportion of soluble phosphate gave larger yields in pot cultures than

[44] J. E. Greaves and E. G. Carter, *Soil Sci.*, 1919, **7**, 121 ; *J.*, 1919, 690A.
[45] *J.*, 1919, 155R.
[46] J. A. Stenius, *J. Ind. Eng. Chem.*, 1919, **11**, 224 ; *J.*, 1919, 265A.
[47] F. S. Fowweather, *J.*, 1919, 111T.
[48] A. Aita, *Annali Chim. Appl.*, 1918, **10**, 45 ; *J.*, 1919, 23A.
[49] *E. g.* C. M. Conder, Eng. Pat. 122709 ; *J.*, 1919, 191A.
[50] *Iron and Steel Inst., Carnegie Schol. Mem.*, 1919 ; *J.*, 1919, 649A.

one containing a lower proportion, and the crop contained a larger proportion of phosphorus. The slag of low solubility, however, had a distinct fertilising effect. Unquestionably the great need at the present time is for investigation into the possibility of enriching the slag at the steel furnace.

Further efforts have been made to explain the remarkable effect of basic slag on grassland. It is evaluated only on its phosphatic content, but the question is periodically raised [51] whether some of the other constituents may not play an important part. J. S. McHargue [52] has suggested that the manganese (of which up to 5% may be present) has a high fertiliser value and supports his view by pot experiments in which distinct crop increases were obtained from manganese carbonate using 5 grms. per 8·5 kilos. of soil (0·028% of Mn). Water culture experiments also show some increases.[53] Experiments in this country, however, have failed to show response to manganese in the field,[54] though definite crop increases were obtained in pots.[55] In Söderbaum's experiments [56] manganese dioxide and ferro-manganese were alike ineffective on oats, though manganese carbonate mixed with aluminium sulphate gave a distinct increase.

Another possibility is that small quantities of fluorides may be beneficial to crops. It is well known that the teeth and epidermal tissues of men and animals contain fluorine which can only have entered the body through the plants eaten as food. All crops contain fluorine (taken from the soil, which contains about 0 03%).[57] but its mere presence in the plant does not prove that it is beneficial : this can only be demonstrated by direct investigation. A. Gautier and P. Clausmann in France showed [58] that small quantities of potassium fluoride are beneficial to plants in pot experiments. and they went further and obtained benefits in field trials also. Applications of 5 kilos. of amorphous calcium fluoride per acre were followed by increases in cereal crops of 5–18%. and sometimes considerably more in the case of root crops.[59]

Other substances might possibly play a part. It was formerly supposed that only few chemical elements were necessary for plant nutrition (nitrogen, phosphorus, potassium, calcium, magnesium,

[51] J. A. Voelcker, *J. Soc. Arts*, 1917, *65*, No. 3356.

[52] *J. Ind. Eng. Chem.*, 1919, 11, 332 ; *J.*, 1919, 332A.

[53] W. E. Brenchley, *Ann. Bot.*, 1910, 24, 571 ; also E. P. Deatrick, *Cornell Univ. Ag. Mem.*, 1919, 19, 371.

[54] *Ann. Rept. Rothamsted Expt. Station*, 1914, 42.

[55] J. A. Voelcker, *J. Roy. Agric. Soc.*, 1903, 64, 348.

[56] H. G. Söderbaum, *Bied. Zentr.*, 1919, 48, 136 ; *J.*, 1919, 507A.

[57] In the form of biotite, apatite, etc. L. A. Steinkoenig, *J. Ind. Eng. Chem.*, 1919, 11, 463 ; *J.*, 1919, 431A.

[58] *Comptes rend.*, 1919, *168*, 976 ; *J.*, 1919, 474A.

[59] *Comptes rend.*, 1919, 169, 115 ; *J.*, 1919, 689A.

sulphur, and iron), but Mazé,[60] working under stricter conditions, has enlarged the list considerably and added boron, aluminium, fluorine, iodine, chlorine, silicon, manganese, and zinc. In ordinary conditions these are all present in the soil in sufficient quantity to meet the very small requirements of the crop, but it is at least arguable that some of them may be absent from the shallow clays on which basic slag acts so remarkably well.

It has already been pointed out (p. 368) that the blast furnace flue dust trials open up the possibility that something may be concerned besides potash—the only conventional fertiliser present.

The influence of barium has been studied by McHargue. It is invariably present in crops,[61] and its carbonate proved beneficial in sand cultures provided sufficient calcium carbonate were present. Strontium carbonate behaved in the same way.[62] Aluminium compounds in certain conditions have proved beneficial.[63] On the other hand magnesium carbonate had no particular value on moor and heath land.[64]

While these results are of interest they are probably of little commercial value at the present time as farmyard manure contains all of these minor substances in sufficient quantity and most of them are present in one or other of the fertilisers used.

It is possible, however, that the fertilising value of sulphates might in certain cases be worth paying for, although in the ordinary way farmers obtain sulphates without additional payment in ammonium sulphate and superphosphate. Numerous experiments have shown them to be effective in promoting plant growth: this year Miller[65] claims a marked response in the case of oats and clover.

Organic Manures.

It has often been supposed that an organic manure is necessarily more effective than an inorganic one as being in some way more natural. There is, of course, nothing in the contention, as a nitrate obtained from any one source is exactly the same thing as the same nitrate obtained from any other. The question can only be settled experimentally. At Rothamsted it is found[66] that the nitrogen of rape cake is not as effective as an equal weight of nitrogen from sodium nitrate or ammonium sulphate in promoting the growth of wheat, barley, or mangolds. Further, rape cake had no residual value excepting apparently on mangolds, and here the observed effects might be traced to the leaves

[60] *Ann. Inst. Pasteur*, 1919, **33**, 139 ; *J.*, 1919, 332A.
[61] J. S. McHargue, *J. Amer. Chem. Soc*, 1913, **35**, 826.
[62] *J. Agric. Res.*, 1919, **16**, 183 ; *J.*, 1919, 332A.
[63] J. Stoklasa and others, *Biochem. Zeits.*, 1918, **91**, 137 ; *J.*, 1919, 113A
[64] B. Tacke, *Bied. Zentr.*, 1919, **48**, 129 ; *J.*, 1919, 507A
[65] H. G. Miller, *J. Agric. Res.*, 1919, **17**, 87 ; *J.*, 1919, 689A.
[66] E. J. Russell, *J. Bd. Agric.*, 1919, **26**, 228 ; *J.*, 1919, 592A

of the mangold crop which are ploughed in. So in the rotation experi-
ments no marked effect was observed after the first year.

BACTERIA ON THE FARM.

The interest taken by soil investigators in bacteria arises from the
great importance of nitrogen compounds for the growth of plants.
Bacteria come into the problem in two ways :

1.- Certain bacteria fix gaseous nitrogen from the air and convert
it into protein. The chemical reactions involved are entirely unknown.
The conditions, however, have been fairly definitely ascertained : a
source of energy such as easily reducible carbohydrates and sufficient
calcium carbonate to ensure a neutral reaction. The process is called
nitrogen fixation.

2. Other bacteria, fungi, etc., decompose protein in the soil with
formation of ammonia, which is subsequently oxidised by bacteria to
form nitrates. This process is called *nitrification.*

The two processes are sometimes confused, but they must be kept
sharply distinct.

Nitrogen fixation is brought about by two types of organisms : (*a*)
those associated with leguminous plants, (*b*) free living organisms.

Numerous attempts have been made to exploit commercially the
action of the nitrogen-fixing bacteria associated with leguminous
crops. The method is to inoculate the soil or the seed with cultures
of the organisms in the hope of securing more active nitrogen fixation.
The importance of the subject cannot easily be overrated and few pro-
positions seem more alluring. Unfortunately the efforts made in this
country have not proved successful. In the United States under rather
different and more hopeful conditions cultures for inoculation of legu-
minous crops are in commerce and apparently have a wide sale. Labora-
tory tests have therefore been devised [67] to allow of some measure of
control. So many failures were obtained by farmers in New Jersey
that the matter was taken up by the Experiment Station [68] ; laboratory
tests showed many of the samples to contain pure and vigorous strains
of nodule organisms. The samples officially obtained were said to be
better than those sent in by farmers. Only a small number of the
organisms presented to a seed, however, are able to produce nodules
on the roots : it is suggested that the effective cells are those possessing
the greatest power of resisting desiccation.[69]

Another reason put forward for the failure of inoculation is the
supposition of Hiltner and Störmer that nodule formation is inhibited
by substances excreted from the seed coat. This view has been tested
in Wisconsin,[70] but no evidence in its favour was found. Meanwhile

[67] H. A. Noyes and C. O. Cromer, *Soil Sci.*, 1918, **6**, 69 ; *J.*, 1918, 777A.

[68] C. R. Fellers, *Soil Sci.*, 1918, **6**, 53 ; *J.*, 1918, 777A.

[69] C. R. Fellers, *Soil Sci.*, 1919, **7**, 217.

[70] A. R. C. Haas and E. B. Fred, *Soil Sci.*, 1919, **7**, 237.

the problem before the manufacturers would be simplified if, as stated by Koch and Butler,[71] a certain amount of cross-inoculation is possible ; i.e., if the same culture could be used for any out of a given list of leguminous plants.

The fixation of nitrogen by free living organisms has been suggested [72] as being more economical than chemical or electrical methods, requiring only waste materials and the sun's energy.

Reference has already been made (p. 370) to the Swedish proposal to produce nitrates by bacterial action from protein compounds.

Decomposition of straw. The value of decomposed straw as manure is well known, but unfortunately straw is so bulky that it cannot easily be handled at a factory. A method has therefore been worked out by Hutchinson and Richards [73] for effecting the conversion of straw into manure by means of bacteria. Large-scale tests of the material are in progress.

Partial sterilisation of soil. Continued investigation is being made at Rothamsted and at the Lea Valley Experiment Station [74] ; in particular it is shown that some of the chloro-derivatives are effective. G. Truffaut, working at Versailles, has successfully used a mixture of calcium sulphide with certain heavy tar oils freed from bases and phenols [75]; the specification states 40% calcium sulphide and 20% each calcium sulphate, calcium phosphate, and heavy oils. A machine for sterilising soil by heat has been designed by the Hon. Rupert Guinness (now Lord Elvedon) and E. H. Richards and patented.[76]

FEEDING STUFFS.

Little has been added to our knowledge of feeding stuffs during the year. Armsby [77] has given a lucid explanation of the meaning of the Kellner starch equivalents now in favour by modern writers on the subject, and has shown their relationship to the older units on which many of us were brought up. The starch equivalent seeks to express the extent to which various foods are able to store energy in new tissues or to prevent the loss of stored energy from the body. They thus serve the same purpose as Armsby and Fries' net energy values, only they are expressed in terms of starch and not in terms of energy. They do not represent the fuel value of the foods nor the content of digestible carbohydrate, actual or potential.

The great practical problem of improving the feeding value of straw still remains unsolved : the German method used during the war is perhaps more significant as a demonstration of the state to which their

[71] G. P. Koch and J. R. Butler, *Soil Sci.*, 1918, **6**, 397.
[72] C. I. T. Doryland, *Abs. Bacteriol*, 1918, **2**, 2 ; *J.*, 1919, 381A.
[73] *Rothamsted Annual Rept.*, 1919.
[74] *Ann. Rept. Nursery and Market Gardeners' Industr. Develop. Soc.*, 1919.
[75] Eng. Pat. 120288 ; *J.*, 1919, 24A.   [76] U.S. Pats. 1303149 and 1303150.
[77] H. P. Armsby and J. A. Fries, *J. Agric. Sci.*, 1919, **9**, 182.

ànimals were reduced than as a permanent solution of the problem. The digested straw is said to have been tolerated by the animals after they were accustomed to it.[78] On the other hand the treatment of straw with hydrochloric acid seems to have effected no improvement in either feeding value or digestibility.[79] Wood cellulose treated with caustic soda gave some kind of a feeding stuff,[80] and beech-nut cake from which the oil had been extracted served to some extent as a war-time food.[81]

The rancidity to which certain cakes become liable has been traced [82] to the activity of lipase in liberating free acids which thereupon oxidise, as suggested by Lewkowitsch,[83] under the influence of air and light ; the change goes on only in presence of moisture. The volatile acids formed from palm-nut cake have a more disagreeable smell than the non-volatile acids from cotton-seed or linseed cakes. Hence palm-nut cake shows the change much more readily than the other cakes.

C. Crowther has discussed the high value of fish meal.[84]

INSECTICIDES AND FUNGICIDES.

A paper by R. L. Mond and C. Heberlein [85] throws important light on the composition of Burgundy mixture and brings out new information which cannot fail to effect improvements in the making of this wash. The fungicidal value of the polysulphide sprays is shown to depend on the proportion of polysulphides present and not on the total sulphur.[86]

An important series of papers on the insecticidal value of chloropicrin has been published by G. Bertrand and others.[87] Unfortunately, however, this substance, while very effective, often presents difficulties in handling which are not entirely overcome.

The promising material obtained by grinding the root of *Derris elliptica* is still under examination, and the principle is shown to be extractible by alcohol.[88]

[78] G. Fingerling, *Landw. Versuchs-Stat.*, 1918, **92**, 1. F. Hansen (*Bied. Zentr.*, 1919, **48**, 110 ; *J.*, 1919, 435A) speaks more highly of the caustic soda process while agreeing (*ibid.*, 118) that the hydrochloric acid process is not good ; *J.*, 1919, 51A. [79] F. Honcamp and E. Blanck, *Landw. Versuchs-Stat.*, 1919, **93**, 175 ; *J.*, 1919, 841A.

[80] G. Fingerling, *Landw. Versuchs-Stat.*, 1918, **92**, 147 ; *J.*, 1919, 841A.

[81] F. Honcamp, *Landw. Versuchs-Stat.*, 1919, **93**, 97 ; *J.*, 1919, 841A.

[82] J. R. Furlong, *J. Agric. Sci.*, 1919, **9**, 137, *J.*, 1919, 384A.

[83] "*Oils, Fats, and Waxes*," 1, 50.

[84] *J. Bd. Agric.*, 1919, **26**, 480 ; *J* , 1919, 735A.

[85] R. L. Mond and C. Heberlein, *Chem. Soc. Trans.*, 1919, **115**, 908 ; *J.*, 1919, 790A.

[86] J. V. Eyre, E. S. Salmon, and L. K. Wormald, *J. Agric. Sci.*, 1919, **9**, 283 ; *J.*, 1919, 843A.

[87] *Comptes rend.*, 1919, **168**, 742, 911 ; and **169**, 880 ; *J.*, 1919, 336A, 437A.

[88] N. E. McIndoo, A. E. Sievers, and W. S. Abbott, *J. Agric. Res.*, 1919, **17**, 177 ; *J.* 1919, 790A.

SUGARS, STARCHES, AND GUMS.

BY JAMES P. OGILVIE,

Technical Editor, " International Sugar Journal," London.

STATISTICAL.

THE most noticeable feature about sugar production since the armistice has been the great rise in the demand, due to the re-entry into the world's markets of the European nations previously restricted by the blockade from purchasing from other than local sources. Consumption has gone up by leaps and bounds, limited only by the ability to obtain the product, and not (as was usually the economic case before the war) by the price asked for it. As the result, prices have been raised to an unprecedented level, which would probably have attained a still greater height under the influence of free competition were it not for the fact that the British and United States Governments had already contracted for a very large proportion of their respective countries' requirements.

It may further be pointed out that whereas the world's present consumption, had there been no war, might have reached 21 million tons (allowing for a 3% increase per annum), the 1918-19 output amounted only to 16,353,730 tons, while the 1919 20 crop is estimated by Willett and Gray [1] at 16,389,394 tons. It is thus clear that consumption has greatly outstripped production.

This deficit is of course mainly due to the collapse of the beet industry, owing to the ravages of war. In 1913-14 (the last complete pre-war year) the world's supply consisted of 9,894,226 tons of cane and 8,845,986 tons of beet, a total of 18,740,212 tons. In 1918-19 the amounts were 11,964,330 tons of cane, but only 4,355,621 tons of beet. This fully explains the present shortage of sugar, and its consequent high price.

Following the reading of the report of the Empire Sugar Supply (Technical) Committee by A. R. Ling [2] (who was Chairman of this Committee), considerable time was devoted to a discussion on the possibilities of expansion of sugar production in the British Empire, in which the Earl of Denbigh, Sir F. Watts, Sir A. Chatterton, Dr. J. A. Voelcker, A. R. Ling, Dr. L. T. Thorne, J. W. Macdonald, W.

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[1] *Intern. Sugar J.,* 1920, 40.   [2] *J.,* 1919, 297T.

Martineau, and others took part. It was concluded that India offered the best field for an increase, though it was recognised that, given a solution of the labour difficulty, British Guiana and Jamaica had possibilities of no mean order. Since that meeting, the Government of India has appointed a commission to inquire into the whole question of the sugar industry in that country, and it is hoped that as the result of this investigation something may be done in this direction. An increase of production to a less degree may also be expected in other parts of the British Empire.

It may be added that there is now the important incentive of a preference on Imperial sugars entering the United Kingdom, amounting to a rebate of one-sixth of the import duty.[3] This is certain to stimulate production, and to encourage the operations of capital.

SUGARS.

The Cane Sugar Industry.

Extraction of the juice by milling.- A steady increase in the extraction figure (sucrose in the juice, per cent. sucrose in the cane) continues to be recorded in different countries.[4] It is, however, in Hawaii that this figure is maintained at its highest, viz. 97·1 for the year 1918, whereas it averaged 93·86 during the period 1909-1917.[5] As was pointed out last year,[6] the excellent results obtained in Hawaii are realised principally by the use of special apparatus for crushing and shredding the cane to a very fine state of disintegration previous to passing it into the train of 3-roller mills. They are also assisted by the use of grooved rollers, as well as by an improved system of macerating the bagasse (or crushed cane) by spraying it with water or weak juice.

By those considering the value of such special appliances, it will be borne in mind that their adoption involves the modification, not only of the milling installation, but also generally of a portion of the rest of the plant, since there is then more juice to be heated and subsided, more " mud " (or insoluble impurities separated in clarification) to be treated in filter-presses, and also more water to be eliminated in the evaporators. More fuel may also be required. It is, therefore, necessary to estimate how much of the additional sucrose passing into the juice will actually be recovered as commercial sugar ; and against the value of this increased yield one must balance items such as the increased capital expenditure, the increased operating costs, the higher rate of depreciation, and lastly the value of any extra fuel (other than bagasse) that may be used.

[3] *Intern. Sugar J.*, 1919, 212, 430.
[4] *Ibid.*, 1919, 282, 302, 386, and 493.
[5] *Ibid.*, 1919, 564.   [6] *Ann. Repts.*, 1918, **3**, 365.

In regard to the question of the increase in the yield, W. Searby [7] believes that about 75–80% of the additional sucrose passing into the juice can be " put into the bags," while data collected by H. Johnson [8] and others support this conclusion. In a discussion of some of the other points at issue, J. N. S. Williams [9] gives an example of the method of calculation employed by him to establish the profit or loss that might result from the installation of improved milling apparatus. The extraction in one of the mills in Hawaii had shown an increase of 1·6% and it was considered that this represented 4 lb. of 96° commercial sugar per ton of cane milled as the gain resulting. The additions had comprised a new boiler, a shredder, three new rollers, and three pairs of mill cheeks, the total expenditure upon which was $32,986. With 120,000 tons of cane for a crop, and with the price of sugar at 6 cents per lb. in New York, the 240 tons of extra sugar yielded net proceeds to the plantation of $23,190. From this sum must be deducted the interest on the increased capital expenditure, the increased cost of bags, and the increased depreciation and repairs, a sum amounting to $17,611, which taken from $23,190 shows a gain of $5576 for the crop. If, however, 100,000 tons of cane had been ground, the extra sugar would have been only 200 tons, and the gain would work out at $1926 at 6 cents. On the other hand, if 100,000 tons of cane were ground, and the price was 5 cents, there would be a loss of $3074 on the undertaking.

These data show that full consideration must be given to all items entering into costs when improved milling installation of the type under discussion is contemplated. They further indicate that the expenditure of large sums of money upon the different new devices is only justified when the factory is milling a large crop of cane ; when the price of sugar is high ; and lastly when the cane is of good average quality, that is, capable of yielding juice of high sucrose content and of high purity.

Clarification of the juice.—At the present time it is almost general practice to clarify the juice coming from the mills by treating it with lime to neutrality or slight alkalinity, heating to boiling point, and subsiding in tanks, the insoluble matter or " mud " obtained being washed in filter-presses until its sucrose content is sufficiently reduced. N. M. Thomas and C. G. Petree [10] now propose a procedure the object of which is entirely to eliminate the use of filter-presses in this way. This is certainly a desirable aim ; and if it were accomplished a considerable saving in labour and cloth, the abolition of the dirtiest department of the factory, and the general simplification of manufacture, would be among the advantages gained.

[7] *Intern. Sugar J.*, 1919, 21.
[8] *Ibid.*, 1919, 17. [9] *Ibid.*, 1919, 20 ; *J.*, 1919, 134R.
[10] U.S. Pat. 1266882 ; *J.*, 1918, 557A. *Intern. Sugar J.*, 1919, 33 ; *J.*, 1919, 134B.

Their process consists in distributing the mud over the cane under-
going crushing by the mills.   Previous attempts to do this have been
made, but these have failed generally because the returned mud
contained more sucrose than the juice present in the cane upon which it
was placed, the efficiency of the extraction process thus being hindered.
According to the new method, the usual routine is so modified as to
produce a mud having a low sucrose content, this being done by treating
the juices coming from the first and second units separately, instead of
clarifying the mixed juice from all the mills as a whole, according to
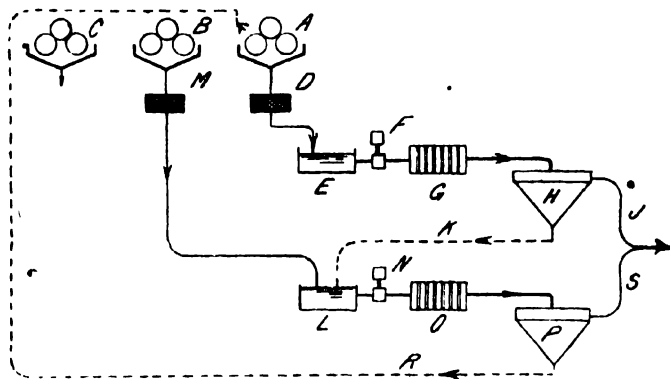
the customary practice.   As is shown in the drawing, the richer juice
expressed by the first unit A of the milling installation is clarified
separately, being limed in the tank E, and pumped through the heater
G into the continuous subsiding tank H,[11] the clear juices resulting
being passed through the line J to the evaporators.   The weaker juice
from the second unit B is treated in the same way.   But the mud from
the bottom of the subsiding tank H is washed by uniting it in the
liming tank L with the weaker juice; while the mud drawn from the
subsiding tank P is sufficiently low in sucrose to be distributed over
the crushed cane passing out of the unit A.   Lastly, to assist the
exhaustion of the crushed cane, water is applied as it passes from unit
B to unit C.

Consideration will show that the success of this procedure will depend
upon several conditions.   Provided that re-solution of certain of the
impurities of the mud does not occur ; that the cane is in a sufficiently
spongy state readily to absorb the mud ; and also that the burning
properties of the bagasse are not adversely affected, this would seem a
modus operandi of much interest to manufacturers, more especially in

[11] *Intern. Sugar J.*, 1919, 246.

countries in which the cost of labour is high. These possible objections
appear to have been successfully met in Australia, as the process has
been adopted by about twenty factories in that country and in Fiji.
Evidence is adduced by those operating it that the juices are at the
present time as high in purity, and at least as clear, as those previously
obtained ; and that, moreover, there is no trouble through clinkering
in the furnaces.

Evaporation of the juice.--During the evaporation of the clarified
juice in the triple- or quadruple-effect apparatus, a certain amount of
matter is thrown out of solution, partly depositing as an incrustation
on the tubes of the plant, and partly remaining in suspension in the
juice, rendering it turbid. One of the conditions of success in the
manufacture of high-grade sugar is that the syrup to be crystallised in
the vacuum pan shall be perfectly clear,[12] though often treatment for
the purpose of realising this is neglected owing to its difficulty. Even
in making ordinary raw sugar for refining the clarification of the syrup
before it passes to the pan is advantageous, since work with the impure
after-products is thereby greatly facilitated.[13]

Syrup resulting from juice which has been clarified simply by treating
with lime, heating, and subsiding, cannot be passed directly through
cloth, owing to its content in gums and pectins. Generally the method
followed in order to eliminate the insoluble impurities is to boil with or
without the addition of lime and sulphurous or phosphoric acid, and to
subside   It is mentioned by C. E. Coates [14] that promising results
have been obtained in Louisiana by a process protected by G. B.
Williamson [15] of treating the syrup with lime and phosphoric acid, and
aerating, the precipitate being thus rendered lighter than the syrup,
from which it is stated to be easily and rapidly separated in a clear
condition. An excellent clarifying effect is also obtained by the Bach
process, which will be discussed later (see p. 389).

Besides the deposition of solid matter, other changes may occur
during concentration of the juice, and certain substances may be
volatilised. It is interesting to note that T. van der Linden [16] has
observed the presence of ammonium carbonate in the water condensed
from the vapour of a multiple-effect evaporator in a Java cane factory,
though he gives no indication of the amount that may be expected
under normal conditions of working. The formation of ammonia
would be explained by the decomposition of proteins during clarifica-
tion. Its presence in the vapours resulting from the heating of limed
cane juice does not appear to have been pointed out previously, though
during the clarification of beet juices the formation of ammonia is very
apparent by its smell in the factory. Regarding the presence of carbon

[12] This vol., p. 389.   [13] *Intern. Sugar J.*, 1919, 578.
[14] *Ibid.*, 1919, 525; *J.*, 1919, 872A.   [15] U.S. Pat. 1317607; *J.*, 1920, 76A.
[16] *Intern. Sugar J.*, 1919, 351; *J.*, 1919, 650A.

dioxide in the condensed water of the cane-sugar house, it is possible that some might have formed as the result of micro-organisms ; while it is also likely that a small amount might result from the decomposition of dextrose and lævulose at the temperature of evaporation. But a more certain cause would appear to be the reaction taking place between the reducing sugars and amino-acids, as pointed out by L. C. Maillard,[17] an effect that has recently been further studied by C. A. Oudemans.[18] This reaction appears to be a condensation in which carbon dioxide and water are eliminated in the proportions CO_2 : $12H_2O$, the former being produced by the breakdown of the carboxyl group of the amino-acid. It will be mentioned later in this report in another connection (see p. 399).
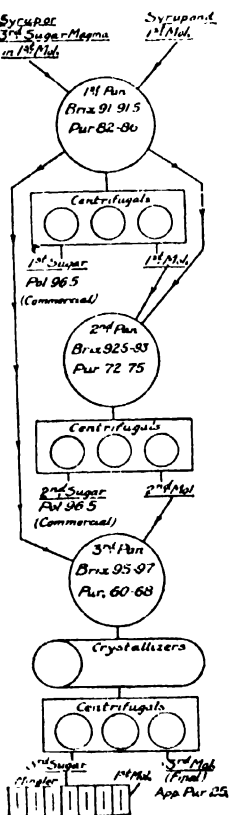
Boiling to grain.—In concentrating the syrup to grain in the vacuum pan to obtain the mixture of crystals and molasses (technically known as " massecuite "), it is no longer general practice to proceed according to the method of repeated boilings, by which crops of crystals are successively obtained from the syrup, the first molasses, and the second molasses. Such a procedure is now recognised to be wasteful of labour, fuel, time, and floor-space, in comparison with the system of " boiling in " the molasses, some modifications of which in present use in Cuba are recorded by R. S. Norris.[19]

This modern method of boiling can best be described by following the details illustrated in the accompanying chart. Three massecuites are obtained, of high, medium, and low purity. In boiling the first, a mixture of syrup and first molasses is used, generally starting the graining on a magma formed of third sugar and first molasses, the proportions being so adjusted that the purity value (sucrose per 100 of dry substance) is about 86% (or perhaps a little lower). On centrifuging the resulting massecuite, commercial sugar polarising about 96° and first molasses having a purity value of about 70% are separated. In boiling the second massecuite, one commences

[17] *Comptes rend.*, 1911, **153**, 1078 ; 1912, **154**, 66 ; *J.*, 1912, 144.
[18] *Interp. Sugar J.*, 1919, 139 ; *J.*, 1919, 154A.   [19] *Ibid.*, *J.*, 1919, 88.

with a " footing" of first massecuite, taken (or " cut ") from the first pan, this boiling being completed with a large proportion of first molasses to give a mixture of about 75% purity. This massecuite on being spun in the centrifugals also gives commercial sugar of about $96°$ polarisation, but the molasses separated is lower in purity than that previously obtained. Lastly, the third massecuite is started by a " cut " from the first pan, which is fed with second molasses to give a mixture of low purity, generally about $60-65\%$: but in order to exhaust the molasses as fully as possible it is gradually cooled in " crystallisers," or tanks provided with slowly revolving stirrers. This final stage gives a low third sugar, which generally is not marketed, but is mixed with first molasses to form " seed " magma, and drawn into the first pan.

In certain of the factories in Cuba the " two massecuite " system of boiling is now in vogue [20]; but it is to be noted that in this scheme both massecuites must be subjected to the crystallisation-in-motion process just mentioned. Thus, the first massecuite is formed of syrup and first molasses to give a purity of about 75%, and after it has been concentrated to the desired density (about 92% of total solids), it is cooled in the crystallisers for 16 hours. At the end of this time, it is centrifuged, being separated into commercial sugar polarising about $96°$ and first molasses of about 47% purity. In boiling the second massecuite, a " footing " of first massecuite is used, and first molasses is drawn in to give a mixture having a purity of about 58%. This, after cooling in crystallisers and centrifuging, gives a second sugar, which is mixed with the first massecuite to be centrifuged with it, while the molasses spun off is " exhausted," having a purity of about 30%.

In the actual operation of effecting crystallisation in the vacuum pan, concentration is continued until the solution becomes supersaturated, at which point the temperature is made to fall, the sugar thus separating as a hardly visible grain. It is now the purpose of the panman to effect the growth of the grain already formed without the formation of small new crystals (known as " false grain "), which operation demands some skill and experience on his part. If false grain be formed the subsequent centrifuging or " curing " of the sugar is greatly impeded, and an inferior product results. Instead, however, of operating in the manner indicated, the practice of " seeding," or drawing a small grained unwashed sugar into the pan to form the nuclei upon which crystallisation can subsequently take place, is largely followed.

A modification of this process of " seeding," which has been found to give improved results in respect of regularity of finished crystal when boiling white granulated, has been described by H. E. Zitkowski.[21] It is an elaboration of a procedure protected as far back as 1865 by J.

[20] *Intern. Sugar J.,* 1919, 89.
[21] *Ibid.,* 1919, 36; *J.,* 1919, 48A.

Lebaudy.[22]   White sugar dust of such a fineness that all passes through
a 100-mesh sieve is used in place of the unwashed sugar ordinarily
added.   Syrup,' or a mixture of syrup and molasses, is concentrated in
the vacuum pan until the solution is slightly supersaturated, at which
point the sugar dust (in amount depending upon the size of the crystal
required) is drawn slowly in, concentration being then continued, and
the usual procedure followed.   Experience with this method of oper-
ating is stated to have shown that, in addition to the greater regularity
and improved colour of the crystal, there is also less liability of the
formation of troublesome false grain.   This last advantage would
apply more particularly to the boiling of low products.   In fact,
W. K. Orth has recently obtained good results with last massecuites
by this procedure in Hawaii.

Centrifuging and finishing.—In separating by means of centrifugals
the mixture of crystals and molasses composing the massecuite—
" curing," as it is most generally called—it is found that the best results
are obtained when the grain is regular and of fair size, and when the
molasses is not very viscous.   " False grain '[*] greatly hinders centri-
fuging by forming with the molasses a viscous mixture that refuses to
penetrate through the wall of sugar lying against the screen of the
machine, and can only be removed by solution in water, a wasteful
expedient.   Only a portion of the false grain is retained in this way,
however, and most of it passes through the holes of the centrifugal gauze
with the molasses, in which it may be lost if the massecuite is a final
one.

This question of the presence of fine crystals in final molasses has
claimed the attention of H. Kalshoven,[23] of the Java Sugar Experiment
Station, who has devised a method for its determination.   He examined
80 exhausted molasses, and found that 26 of these contained more than
10% of fine sugar grain, some having as much as 15 and 17%, the
average of all the samples being 8%.   When it is pointed out that this
amount represents a loss of sugar equal to about 35,000 tons for the
entire production of Java, the importance of the matter is at once
realised.   Several causes may contribute to the presence of these
minute crystals in final molasses.   " False grain " produced during
boiling in the pan by inadvertence on the part of the operator might
account for most of it ; but some might result by centrifuging massecuite
while it is still hot,[24] and by the premature cooling of liquors in pipes
and pumps, which are insufficiently lagged.   Lastly some might form
by cooling massecuites in crystallisers of such a design that the entire
contents do not come under the influence of the stirrers, " dead corners "
being present.

[22] Eng. Pat. 42, 1865.
[23] *Archief Suikerind. Nederl.-Indië*, 1919, **27, 1560** ; *Intern. Sugar J.*, 1919, **608.**
[24] *Intern. Sugar J.*, 1919, 134.

Certain other matters connected with the curing and finishing of the massecuite may be mentioned briefly. In some factories in Hawaii a larger grained sugar is now being made, it being found by P. W. Alston [25] that, since the molasses is thus more easily separated, it is possible to decrease the number of centrifugals in the battery, sometimes by as much as 10%. In the same country, attention has been given to the presence of dark-coloured lumps in the raw sugars produced, and A. B. Melancon [26] considers this irregularity to be due chiefly to " seeding " with low-grade sugar, though it may also be caused by the massecuite adhering to the coils in the pan, as the result of insufficient circulation in the vacuum pan. Sugar often cakes in the bags, and the most usual cause of this defect is the practice of packing the product while still hot,[27] which may conveniently be avoided, according to W. Searby and G. Giacometti,[28] by previously cooling the product in a Hersey drier, through the drum of which air instead of steam is passed. Another source of trouble is the " sweating " of the sugar in the bags, which is believed by J. E. Beila [29] to be likewise due (in the case of cane sugars, at any rate) to the insufficient cooling of the product before packing, though it may be induced sometimes by storing in a damp atmosphere.

Deterioration of raw sugar.—During the storage of the raw sugar, and its shipment to the country in which it is refined, deterioration as the result of the action of micro-organisms may occur under certain conditions. A very thorough examination of this important matter has been made by W. L. Owen,[30] who found that among the organisms effecting this alteration are some closely resembling the so-called potato group, as *B. vulgatus, B. mesentericus, B. liodermus, B. mes. tuber,* and *B. mes. vulgatus,* the most striking points of similarity being the very high power of resistance of their spores to heat, and the ability to form gums, as well as their morphological and physiological characteristics. Torulæ are constantly present. Moulds, as *Aspergillus fumigatus, A. niger,* a blue *Aspergillus,* and *A. pencilloides,* were identified, and owing to their strong inverting power, which they are able to exert in highly concentrated solutions of varying reaction, they form the most dangerous class of micro-organisms to be found in raw sugars. Contrary to the statement made by E. C. Shorey [31] that *Penicillium glaucum* is generally present, it was not possible to identify this organism, although a green mould belonging to the *Aspergillus* group was frequently encountered.

It has been observed by several writers, among them C. A. Browne,[32] that an excellent criterion of the keeping quality of a raw sugar is

[25] *Intern. Sugar J.,* 1919, 135. [26] *Ibid.,* 1919, 173, 177.
[27] This vol., p. 395. [28] *Intern. Sugar J.,* 1919, 179.
[29] *Ibid.,* 1919, 179. [30] *Intern. Sugar J.,* 1919, 277, 334; *J.,* 1919, 549A.
[31] *J.,* 1898, 555. [32] *J. Ind. Eng. Chem.,* 1918, 10, 178; *J.,* 1918, 275A.

afforded by the " factor of safety " (which was first suggested by the
Colonial Sugar Refining Co., of Australia), namely that the quantity,
$W/(100\ S)$, in which W and S are the water and the sucrose contents
respectively, must not be greater than 0·333.[33] As the result of an
examination of a large number of raw sugars of different grades, Owen
is also able to confirm the general validity of this datum. He, however,
observed exceptions, since frequently it was noticeable that a product
with a factor less than 0·333 may undergo more or less change. This
discrepancy is most usually to be observed in cases of sugars which
have been washed with water in the centrifugals. On the other hand,
sometimes sugars having a factor higher than 0·333 may not deteriorate,
examples of this exception being very low-grade sugars, particularly
" seconds." It appears, therefore, that the factor depends to some
extent upon the purity as well as the density of the film of molasses
surrounding the crystals of sugar, a lower factor than 0·333 in the case
of washed sugars, and a higher in that of " seconds " being applicable.

Turning to the practical side of the question, it is of interest to con-
sider the conditions obtaining during manufacture that control to a
greater or less extent the good quality of the finished material. As a
corollary of the " factor of safety " rule, it follows that the film of
molasses surrounding the crystal should be of low purity. In some
countries it is found necessary to wash the sugar with water when
" curing " it in the centrifugals, in order by the removal of some of the
molasses to bring it up to a desired test, generally 96° polarisation.[34]
It is clear that this practice must raise the purity of the film of molasses,
and give a product of greater liability to deterioration under unfavour-
able storage conditions. Difficulty in sufficiently eliminating the
molasses during centrifuging may be caused by the presence of " false
grain," and the importance of avoiding this irregularity, previously
emphasised in another connection,[35] is again apparent. It may also be
due to the molasses being unusually viscous, often the result of an
insufficient clarification, which is another deviation from good practice,
the bad results of which in another direction are mentioned in this
report.[36]

In considering the question of the deterioration of sugar by micro-
organisms, the possibility of carrying out manufacture under aseptic
conditions at once occurs. Useful investigations along this line have
been made by N. and M. Kopeloff.[37] Examination of the products at
the different stages of manufacture showed that, although bacteria
and moulds are present in very large numbers in the raw juice, the
liquid becomes almost sterile after treatment with lime and settling

[33] *Annual Reports*, 1918, **3**, 370.   [34] *Intern. Sugar J.*, 1919, 136.
[35] This vol., p. 384.   [36] This vol., p. 395.
[37] *La. Planter*, 1919, **62**, 237 ; J., 1919, 592A.

(following the usual procedure adopted in clarification). Re-infection, however, took place when later the syrup and massecuite were exposed to the air, especially during centrifuging. It is consequently interesting to note that encouraging results have been obtained by Owen [38] on taking advantage of these observations by covering the tanks, centrifugals, conveyors, cooling bins, etc. This worker has also investigated the possibility of cold storage in preventing or impeding the alteration of sugar, and his laboratory experiments have indicated that deterioration is slight under such conditions, compared with the change occurring at higher temperatures.[39]

Manufacture of plantation white sugar.- One of the most interesting developments taking place during recent years in cane-growing countries is the production on the plantation of a fine white sugar suitable for direct consumption, which can now be made without using animal charcoal, without much extra loss of sugar, without any considerable increase in working expenses, and lastly generally without re-melting. Excellent white sugars, polarising nearly 100°, are now produced in considerable quantity in Java, Louisiana, Mauritius, and to a smaller extent in some other countries. Two essential conditions of success in their manufacture that may be dealt with here are : (1) that the syrup from which the sugar is crystallised shall be of a light colour and a high purity, and (2) that the syrup shall also be free from any insoluble matter

In order to realise the first condition, an exact knowledge of the colouring matters present in the raw juice, as well as of those that may be formed during manufacture, is of much importance. Until recently it was believed that the colouring matters originating from the cane were : (*a*) chlorophyll, which is insoluble, and is readily removed in the process of clarification ; (*b*) anthocyanin, which is soluble, and is precipitated by a large excess of lime (such as is used in the carbonatation process of clarification) ; and (*c*) saccharetin, which is insoluble in the raw juice, but is dissolved by the lime during clarification with the formation of a yellow colour readily bleached by the sulphurous acid with which the juices are generally later treated.

It is, however, now pointed out by M. A. Schneller [40] that another source of colour must receive consideration, namely the so-called " tannins," or polyphenols, which are characterised by giving a blackish-blue or blackish-green colour with a solution of a ferric salt. These substances, the presence of which in cane has been demonstrated by C. A. Browne,[41] are found in the vascular bundles of the eyes, shoots, and tops. Although their content is much less in the mature than in the young plant, the extent to which they occur in the crushed cane of the

[38] *Loc. cit.*   [39] *Loc. cit.*

[40] *Louisiana Bulletin* 157 ; *J.*, 1919, 192A.   [41] *Louisiana Bulletin* 91.

factory may be demonstrated by treating some of this material with a
solution of ferric chloride, when an intense darkening throughout the
mass results.

During the process of milling, these " tannins " pass into the juice,
and a study of their behaviour during this operation has been made by
F. W. Zerban.[42] It would appear from his experiments that they are
first acted upon by an oxidase with the formation of a brown product,
which does not at first change much in intensity when ferrous salts
result from the action of the organic acids of the juice on the iron of the
rollers. Gradually, however, ferric salts are formed by the presence of
peroxidase, and the characteristic dirty-green colour associated with
mill juice at the last stage of crushing later appears. It will be remem-
bered that a similar explanation af the darkening of beet juice has
been advanced. According to M. Gonnermann,[43] catechol is formed
by the action of tyrosinase upon the tyrosine of the beet, this reacting
with the ferrous salts present in the juice, and becoming rapidly con-
verted to the black ferric compound by the action of an oxidase, or
perhaps simply by contact with air.

In regard to the rôle of ferric-polyphenol compounds during the
course of manufacture, M. A. Schneller [44] points out that the colour due
to their presence may be eliminated by their reduction with sulphurous
acid ; but that this effect may not be permanent, as may be observed
by the darkening of a syrup thus treated at its surface in contact with
air. He believes that they account for the slight yellow shade of
plantation white sugars, which may deepen more or less rapidly during
storage. These compounds may, however, be completely eliminated
by an intense system of clarification, such as the carbonatation process,
when they are carried down by the voluminous precipitate formed ;
they are also entirely adsorbed by animal charcoal and by decolorising
carbon. Juice once it has been rendered free of them, Schneller
considers, must subsequently be treated in apparatus (evaporators,
vacuum pans, tanks, pipes, etc.) the interior of which is made of
copper, aluminium, or a suitable rust-proof enamel, in order to obviate
their re-formation.

However, the importance ascribed to ferric-polyphenol compounds by
Schneller and Zerban is not entirely corroborated by W. H. T. Harloff,[45]
an investigator who has had considerable experience in the manufacture
of plantation white sugar. While acknowledging the great interest of
the results obtained by the two American chemists, he points out that
according to experiments made by him in Java, provided that the syrup
be strongly sulphited (which is common practice in that country), the
sugar obtained on crystallisation is generally found to contain only a

[42] *J. Ind. Eng. Chem.*, 1918, **10**, 814 ; *J.*, 1918, 778A.
[43] *Z. Ver. deuts. Zuckerind.*, 1907, **57**, 1068 ; *J.*, 1908., 31.
[44] *Loc. cit.*   [45] *Intern. Sugar J.*, 1919, **574** ; *J.*, 1920, 36A.

slight trace of iron, even though the mother-liquor may have a relatively high content of this element. He believes that the slight yellow shade exhibited by plantation white sugar in bulk is due rather to the dark substances produced by the action of lime during heating upon the dextrose and lævulose present in the juice. Unlike the ferric compounds under consideration, these " glucose " decomposition products cannot be entirely decolorised by sulphurous acid. They have an intense colouring power, the effect of which upon the appearance of the crystals it seems impossible wholly to avoid by any method of treatment at present in practical use.

Coming now to the second condition of success in white sugar manufacture, namely that the syrup before passing into the vacuum pan for crystallisation shall be free from insoluble matter, some particulars may be given of the Bach process,[16] which is at present rather extensively used in Java, and is about to be installed in certain factories in the British West Indies.[17] Its principal advantages are that it effects an excellent clarification of the syrup, that it gives a good yield of white sugar of fine quality, and lastly that it is economical in operation, no special plant other than a sulphur oven and some extra tanks being necessary.

Syrup resulting from the concentration of juice clarified by lime, according to the usual procedure followed in the production of raw sugar, is passed through a cooler in order to reduce its temperature as low as is conveniently possible, after which it is treated with 2–2·5% by volume of milk of lime (at 15° B.), and sulphited to neutrality, using phenolphthalein. Alternatively, the syrup may first be treated with the same quantity of sulphur dioxide, and then with the milk of lime, the clarifying effect as shown by the rise in the degree of purity being the same, though the latter might perhaps be the preferable procedure, as all danger of " glucose " decomposition with the formation of dark products is thus avoided. In either case, the treated syrup with its voluminous precipitate is raised to 90° C. (194° F.), and passed through filter-presses, a brilliant and light-coloured syrup and a firm cake that washes readily being thus obtained. Finally, the filtered syrup is cooled, sulphited to slight acidity to phenolphthalein (say about 0·6–0·9 grm. of SO_2 per litre, an insufficient amount to cause inversion of sucrose), and passed to the pans for crystallisation.

It may be worth mentioning that in this process the conditions are so adjusted that the calcium sulphite crystallises out in microscopic needles ($CaSO_3,2H_2O$), and that when the precipitate is in this form, the effect of the gums adsorbed in impeding the washing of the cake in the presses is very much less apparent than if the calcium sulphite had been in the amorphous state. It may also be of interest to point out

[16] U.S. Pat. 1104095; J., 1914, 935.   [17] Intern. Sugar J., 1919, 613.

in passing that this observation in regard to Bach's process bears out
a fact of some practical importance, which has been recognised in the
sugar industry for some time past, namely, that in the cloth filtration
of gummy syrup the operation is greatly facilitated by the presence of
kieselguhr containing diatoms that are needle-shaped, whereas when
these are mostly circular the rate at which the liquor passes through
the presses or bags is appreciably less.

The Beet Sugar Industry.

British beet sugar. Beet sugar projects at home have continued
during 1919 in the preliminary stage. The Kelham scheme, which has
been developed by the British Sugar Beet Growers' Society under
promise of Government assistance, has had to devote most of its acreage
to cereals pending the acquisition of beet seed and the erection of a
factory. At the annual meeting in December, however, the Society
were able to announce that the estate had been so cultivated and
cleaned that they were ready at any moment to begin to grow sugar
beet for the factory to be built before the autumn of 1921. It would
seem therefore that the Society expect to start their first operations
during the 1921 22 campaign, in which event their first sugar should
be on the market in about two years' time. A new company is being
formed under the name of Home Grown Sugar, Limited, to acquire
from the Society the assets of the business ; and it is appealing to the
public for a subscription of £250,000, which sum with a like amount
promised by the Government will provide the new concern with a
working capital of £500,000. Members of the British Sugar Beet
Growers' Society have subscribed largely for the new issue.

Apart from Kelham, the only other possible source of sugar production
in England is Cantley. During the year an effort appears to have been
made to reorganise the company controlling the factory with the help,
it is reported, of some foreign capital and technical assistance ; but
so far no definite announcement regarding the success of the *pour-
parlers* has been made.

As the present preference on home-grown beet sugar (polarising 98°)
works out at 6s. 2⅝d. per cwt. compared with the foreign beet product,
and at 2s. 4d. per cwt. compared with Imperial cane sugar, there is
considerable fiscal incentive to extend the beet sugar industry in the
United Kingdom.

Manufacture. During the period under review, little has been
published on the Continent in regard to the technology of beet sugar
manufacture, conditions in this industry having there declined to a
low level. It is reported by a well-known writer (in Holland) that
no plans for extension or improvement have lately been formulated ;
and that the outlook, particularly in Germany and France, is such as
to cause considerable despondency. In consequence, it is impossible

here to construct a connected narrative of progress effected in the several stages of manufacture, as has been done in the case of the sister industry, though a few papers published on the Continent and in America may be noticed briefly.

In the clarification of beet juices by the carbonatation process, it is usual to add the lime after raising the liquid to a temperature of 65°–70° C. Some loss of sucrose owing to hydrolysis by the organic acids present may occur in this way, and for this reason, and also to improve matters when the juice is particularly impure, some of the full quantity of lime may be added before passing the juice to the heaters. E. Psenicka [48] now states that a very satisfactory clarifying effect may be obtained by the addition to the cold juice of a quantity of the calcium carbonate precipitate, previous to heating, liming, and carbonating. This is best done by returning 4·20% of the unfiltered carbonated juice to the raw juice. It is claimed that in this procedure the darkening which frequently occurs when the juice is limed in the cold is obviated ; that inversion is prevented ; that after liming and carbonating a very granular precipitate, which filters readily, is obtained ; and lastly that a saving in lime can be effected. Little alteration of the plant is required ; and this appears to be a modification worthy of trial especially when dealing with juices in the clarification of which some difficulty is being experienced.

In present practice, filter-presses are always employed to separate the precipitate produced in the carbonatation process ; but it is of interest to notice in an article by B. Bloch [49] that the possibility of using centrifugals is now being discussed in Germany. Already in certain cane-growing countries encouraging results have been obtained in this direction,[50] though in some of the experiments made trouble has been encountered on account of the slimy nature of the mud, which prevented continuous action. In the beet factory, however, the precipitate is in a more favourable condition, owing to the excess of calcium carbonate it contains, but a disadvantage that would remain is the rather high power consumption required.

When the price of sugar is high, it is worth while treating the final molasses obtained in the factory for the extraction of the sugar that cannot further be separated by concentration. In America, the calcium saccharate method is largely used for this purpose, and as the literature of this operation is rather meagre, some details given by C. J. Leonis [51] in regard to the conditions for realising the best yield will be welcomed by those concerned with the process. It is advised first to dilute the product with wash-water to a suitable sucrose con-

[48] Z. Zuckerind. Böhm., 1919, 43, 224 ; J., 1919, 592A.
[49] Z. Ver. deuts. Zuckerind., 1918, 383 ; J., 1919, 550A.
[50] Ann. Repts., 1918, 3, 367.
[51] Sugar, 1918, 20, 15, 56 ; J., 1919, 49A.

tent, and add milk of lime at 35° Brix at the rate of 18 parts of calcium oxide per 100 of sucrose present, that is, sufficient to form the mono- and some di-saccharate. In order to precipitate the insoluble tri- saccharate, powdered lime is added, gradually at 12°–13° C., preferably in a special cooler under pressure, taking care not to allow the temperature to rise above 14° C., the addition being stopped when the density of the filtered solution corresponds to 6·5° Brix. The precipitate of tri-saccharate is separated in a filter-press, washed with water containing a little milk of lime, discharged, diluted with a little sweet-water, and finally sent to the carbonation tanks, where it is decomposed, the liberated sucrose being united with that in the juice undergoing clarification.

Beet sugar factories in the United States produce a granulated white sugar which is sold for direct consumption without refining, and occasionally on dissolving this product in water a white turbidity is formed. It is explained by C. J. Leonis [52] that this may be traced to lack of care during sulphitation, calcium bisulphite having passed into the filtered syrups, and having been subsequently decomposed to calcium sulphite during boiling in the pan or drying in the granulator. Again, if the sulphited syrups are insufficiently heated amorphous calcium sulphite is produced, and may pass through the filter-cloths. It may sometimes happen that such white beet sugars show a slight turbidity when recently made, but less after storage for 90 days or more. This is explained by the presence in the sugar of free sulphurous acid, which slowly transforms the calcium sulphite into the acid salt; or it may also be due to the oxidation of calcium sulphite into the more readily soluble calcium sulphate.

The Refining Industry.

Decolorising carbons.- Animal charcoal (bone-black) has been in use in sugar refining since about 1812, and the first British patent relating to its application in this connection was granted to P. and J. Mar- tineau [53] in 1815. From time to time efforts have been made to replace this material by decolorising carbons, which may possess a much greater power of adsorbing impurities (particularly colouring substances) from solutions of raw sugars, and may also be regenerated.

During the past few years, numerous trials in this direction have been carried out with the preparation " Norit " (which is made in Holland by a secret process), and it is reported that this carbon, as well as the protected method of using it, [54] is now in continuous oper-

[52] *Sugar*, 1918, **20**, 357 ; *Intern. Sugar J.*, 1919, 249 ; *J.*, 1919, 432A.

[53] Eng. Pat. 3912, 1815.

[54] Eng. Pat. 21204, 1911 ; *J.*, 1912, 1047 ; Eng. Pat. 11860, 1912 ; *J.*, 1913, 376 ; Eng. Pat. 3854, 1915 ; *J.*, 1916, 432.

ation in large factories in Holland, America, and elsewhere, in the production of refined sugar. Improved methods of revivification have recently been introduced, using a specially designed furnace,[55] which is stated to operate easily and economically ; while it is also claimed that the difficulty previously experienced in regard to obtaining the filtrate perfectly free from black particles [56] has also been overcome.

Much work continues to be done with the object of producing a decolorising carbon that is both cheap and efficient. Generally, in its preparation sawdust or other carbonaceous material is charred in the presence of an " impregnating substance " (e.g. lime), and heated to redness, the mineral matter being finally removed. A valuable systematic study of the comparative value of a large number of impregnating substances has been made by F. W. Zerban, E. C. Freeland, and D. D. Sullivant,[57] of the Louisiana Experiment Station, in which the sawdust of yellow pine wood was mixed to a paste with the added compound, dried, and carbonised with exclusion of air, being finally heated to about 900° C. for 2 hours. Assuming the decolorising power of " Norit " to be 100, the comparative efficiency of some of the carbons obtained with the use of different substances was found to be as follows : sodium carbonate, 19 ; sodium sulphate, 51 ; sodium chloride, 22 ; ammonium sulphate, 37 ; silica, 39 ; calcium chloride with excess of ammonium chloride, 48 ; calcium sulphate, 173 ; aluminium chloride with excess of ammonium chloride, 86 ; calcium carbonate, 103 ; aluminium hydroxide, 238 ; barium hydroxide, 292 ; stannous chloride, 292 ; magnesium hydroxide, 422 ; zinc chloride, 175 ; and magnesium chloride with an excess of ammonium chloride, 3200. Regarding the amount of the impregnating substance, it should be mentioned that the basis chosen was 1 part by weight of sawdust to 1 of calcium oxide, the other compounds used generally being taken in equivalent proportion.

It is possible as the result of these experiments to formulate certain general conclusions in regard to the value of the several reagents used. Thus it would seem that the most important condition is the state of aggregation of the impregnating substance during the final heating to about 900° C., compounds that are either solid (as lime) or gaseous (as zinc or magnesium chlorides) at this temperature producing good carbons ; whereas those that are liquid (as sodium hydroxide or carbonate) give an unsatisfactory result. Other conditions being equal, compounds having the greatest chemical energy appear to form the best impregnating substances, anhydrous magnesium chloride, for example, being superior in this respect to zinc chloride, the heat of solution of which is only about two-thirds that of the former salt.

[55] Eng. Pat. 104456 ; J., 1917, 445.   [56] Ann. Repts , 1918, 3, 373.
[57] Louisiana Bulletin, 167 ; J., 1919, 873A ; also J., 1919, 527A ; 1918, 480A.

It is further to be concluded from these useful results of Zerban and his collaborators that the cost of making a carbon having a sufficiently high decolorising power must necessarily be considerable when following such methods. A large amount of impregnating substance is required ; and if this is insoluble in water, the quantity of acid (generally hydrochloric) for its elimination is a considerable item ; while again it must be borne in mind that the actual yield of carbon (even when no loss by oxidation occurs) is rather small.

Several patents relating to processes of preparing decolorising carbon have recently been taken out ; but from the point of view under discussion, that of economy of production, one of the most interesting is that of the Ensuiko Seito Takushoku Kabushiki Kaisha.[58] In this specification it is stated that it has been found unnecessary to add any impregnating substance previous to heating. If the structure of the carbonaceous material be sufficiently well disintegrated, its saturation with water alone previous to charring suffices for the production of a carbon of high power. Such a method of preparation (if efficient) would be much more economical than most of those yet proposed. Another process that appears to be of some interest is that protected by S. S. Peck,[59] in which a mixture of molasses and kieselguhr is heated in the presence of sulphuric acid, and finally washed with water. Decolorising carbon thus produced is in large scale operation on the Kahuku plantation, Oahu, T.H., for the production of a white sugar for direct local consumption. Future work on the production of decolorising carbons will probably concentrate upon processes, such as the last two mentioned, which obviate the use of the large amount of impregnating substance and of acid for its subsequent removal, hitherto generally believed to be necessary.

Defective sugars for refining. At the recent conference on the production of sugar within the British Empire, J. W. Macdonald [60] drew attention to the defective nature of certain sugars imported into this country from Cuba during the war, pointing out that although the manufacturers of such products may have saved themselves a trifling sum by the adoption of careless methods (*e.g.* packing hot, so that a solid mass had formed), it had cost refiners on this side a considerable amount to rectify the results. This censure of practices that render refining unnecessarily difficult could be endorsed by other refiners. There can be little doubt that, while some manufacturers produce excellent grades for refining, others appear to operate without sufficient care, and without always bearing in mind the requirements of the purchasers of their wares.

A good raw sugar, in addition to possessing a fairly high sucrose content (say, 96–98%), should have a grain that is regular but not too

[58] Eng. Pat. 117828 ; *J.*, 1918, 599a.
[59] U.S. Pat. 1251546 ; *J.*, 1918, 133a ; 1919, 192a.   [60] *J.*, 1919, 313t.

small, in order that it may readily be washed in the centrifugals (the first step in refining). Especially should it be free from ",false grain," the cause of the formation of which has already been discussed,[61] as has also that of the " caking " of the•product in the bags.[62] Further, it should not contain an undue amount of colouring matters (particularly caramel, which is reluctantly adsorbed by animal charcoal), nor should the molasses surrounding the crystals be.very viscous. These are the most desirable characteristics of a raw sugar, and if it were possible on the part of manufacturers uniformly to turn out products of the type indicated, it is certain that the work of the refiner would be rendered considerably lighter than it has been during the past few years.

Perhaps the operation in the manufacture of raw sugar upon which the realisation of an improvement of its refining quality is more dependent than any other is that of clarification. Recently W. D. Horne[63] visited Cuba on behalf of American refiners, in order to study the question of the defective raw sugars which some of the factories there have been producing, and he made certain recommendations in regard to the practice of clarification that are worthy of notice by manufacturers as a whole. He pointed out that the exact adjustment of the amount of lime used in this operation is of greater importance upon the quality of the sugar produced than appears generally to be thought. Addition to neutrality to litmus, although it inhibits inversion during boiling, does not effect the complete precipitation of albuminoids and gums, so that settling is difficult, and the syrup resulting on concentration is viscous. If the amount be continued until alkalinity to phenolphthalein is indicated (usually 2·3 times as much) a greater amount of impurities is thrown out of solution, but a notable increase of colour results later during heating and evaporation, owing to the action of the alkali upon the reducing sugars present in the juice. He therefore advised the *via media* of liming to a " moderate degree of alkalinity, varying from one-third to two-thirds of the way from litmus to phenolphthalein alkalinity." This was found generally to result in a satisfactory defecation of the juice. Nevertheless, care must be taken that the subsequent heating (to effect the maximum precipitation previous to settling) is not unduly prolonged, otherwise a marked increase in the colour will inevitably result.

Another desirable quality that a raw sugar should possess is that after being washed in the centrifugals in the refinery to remove the adhering molasses, the crystals remaining should be as white as possible. If they are highly coloured (as sometimes happens), the comparatively dark syrup resulting from their solution will unnecessarily diminish the capacity of the char filters. This point has been studied by W. R.

[61] This vol., p. 383.   [62] This vol., p. 385.
[63] *Intern. Sugar J.*, 1919, 462, 464.

McAllep,[44] who observed that in one of the factories in Hawaii a sugar was being made which, though of excellently formed grain, was particularly dark throughout. He concluded this defect largely to be due to the system of " seeding " with low-grade third sugar in the vacuum pan, so that crystals were caused to grow upon a particularly dark nucleus (following the procedure outlined in another part of this report [45]). Greatly improved results were obtained by first forming the grain in the comparatively pure syrup, instead of in a mixture of syrup and molasses ; then building upon these crystals by drawing further charges of syrup or molasses into the pan. Regarding the third sugar produced, being no longer used for " seed," this was either remelted in the juice, and the resulting solution drawn into the last vessel of the multiple-effect evaporator, or else mixed in the crystallisers with the higher grade massecuite. However, " seeding " with third sugar need not necessarily be condemned generally, though the practice is certainly reprehensible in the case under consideration, in which the products were unusually dark. If in this particular factory care had been taken to prevent the formation of coloured " glucose " decomposition products (by avoiding an excess of lime), and of caramel (by abandoning the use of live steam for heating the molasses previous to drawing it into the pan), it is probable that the detrimental effects of the practice would have been greatly minimised. But to what extent, could only have been decided by further investigation.

Analysis of Sugar Products, and the Results of Chemical Control.

Determination of sucrose —Under this heading may be considered the proposal made by certain chemists in America to adopt a new standard weight for the saccharimeter (or polariscope equipped with a scale permitting the reading of the sucrose per cent. directly). At the present time the standard adopted universally (except in France and Mauritius) is the weight of 26·0 grms. of sucrose dissolved in 100 metric c.c. at 20° C., which solution when observed in a 200 mm. tube at 20° C. gives a reading of 100°. It is believed by C. A. Browne [66] and others [67] that the time is opportune " to get away from the illogical and inaccurate German scale," and to adopt another, preferably that of 20 grms., which was first proposed in 1896 by D. Sidersky,[68] supported by H. Pellet [69] and by F. Dupont,[70] and is already in use to some extent in France.

In support of this proposal, it is argued : (*a*) that the present 26·0

[44] *Intern. Sugar J.*, 1919, 522 ; *J.*, 1919, 784A.   [45] This vol., p. 382.
[66] *Intern. Sugar J.*, 1919, 85, 128.
[67] *Ibid.*, 1919, 463 ; *J.*, 1919, 593A.
[68] *Reports of Second Intern. Congress Appl. Chem.*, Paris, 1896, 2, 391.
[69] *Ibid.*, 516.
[70] *Reports of Fifth Intern. Congress Appl. Chem.*, Berlin, 1903, 8, 129.

grm. standard has been shown to be inaccurate [71] ; (b) that 20 grms. is a value offering certain conveniences in use (e.g. it gives results that are readily converted into percentages) ; and (c) that 20 grms. is a compromise between 26·0 and 16·29, which latter is the weight generally used in France at present.

Although chemists in the United States, Hawaii, and Cuba have in the main expressed themselves in favour of the adoption of the proposal, there are some dissentients. F. Bates,[72] of the Bureau of Standards, Washington, for example, controverts the arguments that have been offered " to bring about so momentous a change as a new normal weight," holding that the present standard of 26·0 grms. should be retained in operation : (a) because it is already in almost universal use ; (b) because its rejection would necessitate the re-standardising of all instruments now in use (this involving the re-cutting of the quartz wedges, and the re-calibration of the scale), which would be difficult, and " in practice would never be done " ; (c) because the adoption of a new standard would demand the recompilation of the tables correlating the specific gravity, polarisation, and sucrose percentage of juices and syrups ; (d) because in effecting the polarisation of raw sugars the accuracy of the reading would be decreased to $\frac{1}{50}$ or nearly $\frac{1}{40}$—of that at present realised ; and (e) because unless Great Britain and her Colonies, Central Europe, South America, and Java all accept the new standard, the international situation in regard to comparative tests would be rendered difficult and uncertain.

This question has aroused much discussion among chemists in the sugar world. In France, the Association des Chimistes de Sucrerie [73] has decided " to support Dr. Browne in accomplishing the adoption of the 20 grm. weight " ; while in this country, and in sugar-producing parts of the Empire, steps are being taken to obtain a decision in the matter.

Determination of reducing sugars.- It is generally agreed that in the determination of reducing sugars by means of Fehling's solution the most accurate results are obtained by filtering off the cuprous oxide, and weighing it as metallic copper. Modifications of this method, depending upon the volumetric determination of the copper, either in the precipitated cuprous oxide after separation by filtration, or in the unreduced Fehling's solution, are largely followed on account of greater rapidity, and certain processes have been elaborated which in careful hands give results closely approaching those obtained by the gravimetric method.

One of the best known of these volumetric modifications is that in which the separated cuprous oxide is dissolved in a solution of a ferric

[71] *Scientific Paper No. 268, Bureau of Standards*; *J.*, 1916, 1126; 1919, 873A.
[72] *Intern. Sugar J.*, 1919, 408; *J.*, 1919, 593A.
[73] *Intern. Sugar J.*, 1919, 573.

salt, and the resulting reduction ascertained by titration with standard permanganate solution. It is employed in France, Java, and elsewhere in factory control work, being both rapid and reasonably accurate. According to the routine recently described by Bettinger,[74] after boiling together the sugar and Fehling's solutions, the cuprous oxide is washed quickly by decantation, and the washings passed through a Gooch crucible provided with an asbestos pad. Standardised ferric sulphate solution is added to the precipitate remaining in the reduction flask, which is immediately connected by means of a rubber stopper to a filter-pump. A further known volume of the ferric sulphate solutions is added to the Gooch crucible, in order to dissolve the cuprous oxide retained on the pad, and the liquid is drawn into the flask. Finally, after washing the crucible with water, the solution in the flask is titrated with permanganate. This modification should prove somewhat more rapid and convenient than the procedure originally prescribed by G. Bertrand,[75] hitherto generally followed, since the same flask is now used throughout, and the use of a Soxhlet filter-tube abandoned. It is stated that the entire operation of determining reducing sugars by this process, including reduction, decantation, filtration, and titration, can be performed in about 20 minutes; while it is further claimed that the error involved should not be more than 1·2%, as compared with the gravimetric method.

A volumetric process, possessing the marked advantage of obviating the necessity of separating the precipitated cuprous oxide from the excess of Fehling's solution, has been elaborated by F. M. Scales[76] and W. B. Clark.[77] A modified Fehling's solution,[78] containing copper sulphate, sodium citrate, and sodium carbonate, is employed. After reduction has been effected, the liquid is acidified with acetic acid, a known excess of standard iodine solution added, and the cuprous oxide dissolved by the addition of a small quantity of hydrochloric acid. Finally, the excess of iodine remaining after that required to convert the cuprous chloride to cupric iodide is titrated with thiosulphate. As finally modified by Scales,[79] this method may be carried out in one flask, and it should prove a rapid and convenient procedure for routine practice.

Ash.— It has previously been pointed out that for the conversion of the sulphated to the so-called " true " or carbonated ash the deduction of 10% generally applied can hardly be held to be exact. This is again emphasised by H. I. Waterman and Miss H. de Wijs,[80] who found in

[74] *Bull. Assoc. Chim. Sucr.*, 1918, **35**, 111 ; *J.*, 1919, 381A.
[75] *Bull. Soc. Chim.*, 1906, **35**, 1285 ; *J.*, 1907, 60.
[76] *J. Biol. Chem.*, 1915, **23**, 81 ; *J.*, 1915, 1264.
[77] *J. Amer. Chem. Soc.*, 1918, **40**, 1759 ; *J.*, 1919, 85A.
[78] *J.*, 1907, 1102 ; 1911, 439.
[79] *J. Ind. Eng. Chem.*, 1919, **11**, 747 ; *J.*, 1919, 785A.
[80] *Chem. Weekblad*, 1919, **16**, 885 ; *J.*, 1919, 593A

the case of beet products that the value is about 20%, which confirms the results obtained by Ogilvie and Lindfield reported last year.[81] In the same paper, these Dutch writers show that the rapid method of determining the ash of sugar products proposed by Wagenaar (carbonising a concentrated solution drop by drop in a heated platinum dish. and finally incinerating over a Teclu bruner) yields insufficiently precise results. owing to the volatilisation of the alkali salts.

Dry substance.— One of the most troublesome operations with which the sugar chemist is confronted is the exact determination of the total solid matter present in molasses or other impure factory or refinery products. At the present time, the so-called "true" dry substance (as distinguished from the "apparent" value, given by the hydrometer) is found by the desiccation method. which. though it may be reasonably reliable in the case of the purer products, is generally recognised still to leave something to be desired in the case of cane molasses. Such impure products are susceptible to decomposition during desiccation under ordinary conditions of working (such as drying on sand or bibulous paper at 102° 105° C.) ; and this is due either to the decomposition of the lævulose present. or to the reaction taking place between reducing sugars and amino-acids, carbon dioxide being evolved.[82] Probably loss of solid matter is to be attributed to both of the causes suggested.

Experiments with the purpose of diminishing as far as possible this source of error have been carried out by C. A. Browne.[83] Desiccation was effected over phosphorus pentoxide *in vacuo* at a temperature not exceeding 70° C.. using an oven with glass windows. It was found by carefully manipulating the vacuum in the early stages of drying that it was possible to cause the material to foam up sufficiently to leave the residue in a porous condition, so that the removal of the last traces of moisture was rendered easy.

Such determinations admittedly are tedious, and it is therefore proposed by J. P. Ogilvie and J. H. Lindfield[84] that in routine factory work advantage should be taken of the principle involving the use of a solution factor, as first proposed by C. O'Sullivan.[85] This suggestion would be put into practice, firstly by ascertaining the dry substance of the particular product by a method believed to give results most closely approximating to the truth (such as that now proposed by Browne), and secondly by determining the specific gravity at the prevailing laboratory temperature of a solution of the product containing 10 or 20 grms. of actual dry substance in solution. This value would give the solution factor of the particular class of product at the temperature and concentration chosen ; and factors would in this

[81] *Ann. Repts.*, 1918, 3, 380.   [82] This vol., p. 382.
[83] *Intern. Sugar J.*, 1919, 599.   [84] *Ibid.*, 1919, 398 ; *J.*, 1919, 650A.
[85] *J. Chem. Soc.*, 1876, ii, 125.

manner be established for syrups, massecuites, and molasses. In the case of any particular class of product (molasses, for example), the mutual proportions of sucrose, reducing sugars, organic non-sugars, and ash controlling the factor do not vary throughout the season to an extent sufficient appreciably to disturb it. In place, therefore, of determining the true dry substance directly by desiccation in every sample, one such desiccation determination (in order to establish the factor) would suffice in the examination of a large number.

Chemical control results.— In certain countries, Java, Mauritius, and Hawaii, for example, all the factories take part in a scheme for the compilation of chemical data, which subsequently are published and distributed for the purpose of comparison. This system of " mutual chemical control " has proved of the greatest utility in indicating the efficiency of every operation in every factory in the country concerned, and particularly in demonstrating the value of any modifications in milling, clarification, and boiling that are introduced.

It is of interest, for example, to compare the control figures relating to different stages of manufacture in the case of one of the factories in the progressive sugar-producing country of Hawaii,[86] selecting the years 1911 and 1918, during which period a considerable improvement in several operations had been effected. Milling extraction (sucrose in the juice, per cent. sucrose in the cane). 92·9, 97·9 , sucrose left in the crushed cane or bagasse, per cent., 3·4, 1·2 ; water in the bagasse, per cent., 47·4, 36·1 ; recovery of commercial sugar, per cent. sucrose in the juice, 84·3, 90·5 ; total losses, per cent. sucrose in the juice, 15·7, 9·5 ; sucrose lost in the bagasse, 7·4, 2·1 ; sucrose lost in the press-cake, 0·35, 0·20 ; and sucrose lost in the molasses. 8·25, 7·20.

These data indicate a remarkably high present state of efficiency (which well may be emulated in other countries), both in respect of milling and the recovery of commercial sugar from the juice. It is especially noticeable that the recovery of sugar from the juice had kept pace with the extraction of juice by the mills, contrary to the belief formerly held by many that an increase in the extraction beyond about 95 would be without result in the final yield, owing to the greater proportion of impurities inhibiting crystallisation thus introduced. It is further to be observed that better methods of washing the clarification mud in the filter-presses had been put into operation. Another point worthy of emphasis is that in spite of the amount of water used for spraying the crushed cane or bagasse in order to exhaust it being doubled, no extra fuel had been required to deal with the increased volume of the juice in the evaporators. This was due principally to the improved efficiency of the evaporation plant, but also to a more careful supervision of the burning of the bagasse in the furnaces, and to the more effective insulation of surfaces radiating heat.

[86] *J. Chem. Soc.*, 1919, 576

Some of the figures obtained during the past decade in Mauritius [87] are also worth comparing, in order to show the excellent progress made in that country. In former years the proportion of white first-grade sugar (which is known as *vesou*) was about 72–75% of the total production, the remainder being in the form of yellow and brown sugars. After the installation of crystallisers in the factories, this figure reached 80–82%; while later, as the result of "double curing" (centrifuging the massecuite, discharging, mixing with light-coloured syrup, and again spinning), the amount rose to 94–95%. At the present time, due to the sulphitation of the syrups before graining and to better methods of separating the molasses, the greater number of factories in the island are producing 95–99% of first-grade white crystals per 100 lb. of sugar made. It is also to be seen that now the extraction of sugar in the juice has reached 94–95% of the sucrose in the cane, this being attributed largely to the grooving of the mill rollers. Similarly interesting results will be revealed by a study of the latest control data published in Java,[88] Cuba,[89] Natal and Zululand.[90]

STARCHES AND GUMS.

Starches.—A colourless solution of dextrin, mobile at ordinary temperatures, and ready for use as an adhesive without the addition of water, is prepared by W. W. McLaurin [91] by treating commercially pure starch with an equal quantity of water and about 0·001% (of the weight of starch) of acid, *e.g.* hydrochloric acid, in a closed vessel, this mixture being subjected to the action of steam at a temperature of 138° C. (280° F.). In a subsequent specification,[92] the same inventor makes claim for the preparation made according to the procedure just described. It has a concentration of about 50%, and contains less than 10% of sugars calculated on the weight of the dry product. In addition to being used as an adhesive, it is applicable without further treatment as a coating or an impregnating material for paper, textiles, wood, etc.

In order to produce an adhesive which on drying gives a clear and thin film, C. Bergquist [93] proposes to heat a mixture of starch and water with acid to make a "thin boiling," at which point a small quantity of formaldehyde is added and an ammonium salt to form hexamethylenetetramine. An adhesive capable of flowing readily through pipes less than 2 in. in diam., for application to surfaces by means of suitable spreading devices, can be made, according to J. B. B.

[87] *Intern. Sugar J.*, 1919, 282, 302.   [88] *Ibid.*, 1919, 386.
[89] *Ibid.*, 1919, 339.   [90] *Ibid.*, 1919, 191.
[91] U.S. Pat. 1283839; *J.*, 1919, 86A.
[92] U.S. Pat. 1284120; *J.*, 1919, 86A.
[93] U.S. Pat. 1287841; *J.*, 1919, 193A.

Stryker,[94] by mixing raw cassava starch with water and a degenerated starch so as to attain a certain viscosity, this mixture being treated with caustic alkali to form a homogeneous solution.   F. B. La Forge [95] makes claim for the method of preparing a useful adhesive, in which corn (maize) cobs are heated under pressure with water, and the resulting colloidal solution separated from the residue and concentrated to the consistence of a thick syrup.

Gums.—Karaya and other insoluble gums of the East Indian and Persian type are converted into a soluble form, according to a process protected by the Calico Printers' Association, J. B. Fothergill, and G. W. Wilson,[96] by treating with a solution of sodium or potassium peroxide, percarbonate, persulphate, or persilicate, and the solution subsequently neutralised and bleached, if necessary.   For example, 160 lb. of powdered karaya gum is stirred into 40 gallons of water containing 8 oz. of sodium peroxide.   After about $1\frac{1}{2}$ hours a solution of 9 oz. of sodium peroxide in 5 gallons of water is added, and the liquid is heated and boiled for 3-4 hours, cooled, neutralised with hydrochloric acid, diluted to 80 gallons, and finally clarified.   When used for textile finishing, the solution of gum thus prepared may be bleached with hypochlorites.

[94] U.S. Pat. 1299809 ; *J.*, 1919, 433A.
[95] U.S. Pat. 1285247 ; *J.*, 1919, 114A.
[96] Eng. Pat. 120183 ; *J.*, 1919, 10A.

FERMENTATION INDUSTRIES—1918.

By L. T. Thorne,

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The great restriction of the production of beer referred to in the 1917 report as introduced in 1917 was continued and even carried further during 1918, and the total quantity (standard barrels) allowed to be brewed was considerably less than one-third of the normal, pre-war production. It was also enacted that, whilst no brewer should brew any beer at his brewery at an original gravity below 1010°, the *average* gravity of the beer brewed in any quarter should not exceed 1030° in the United Kingdom, or 1045° in Ireland. In America restriction took the form of reduction of materials used to 70% of those used in 1917, and the limitation of the alcohol content of such malt liquors, " ale and porter excepted," to a maximum of 2·75% of alcohol by weight (*i.e.* 5·58% proof spirit). In Germany and Austria far more drastic restriction was enforced, the original gravities of the beers being often under 1010°. The result of these conditions has been to make brewing technologists devote the closest attention to the production of these low-gravity " war beers," and this has met with considerable success. The same causes have proved a very great stimulus, also, to work on the so-called " non-alcoholic beers," or cereal beverages containing less than the 2% of proof spirit allowed for non-excisable fermented beverages. Here again considerable success has been attained (especially where glucose forms a considerable constituent of the wort), and presentable beverages have been produced. But neither these nor the very low-gravity beers have the palate-fullness and flavour of pre-war light and draught beers, and both brewers and consumers are calling for relaxation in the restrictions and a return to beers of a more reasonable gravity. It may well be, however, that beers of somewhat lighter gravity than in pre-war times will be popular.

ENZYMIC ACTION.

Much valuable work was published in 1918 on this subject. E. W. Rockwood [1] finds that *a*-amino acids, whether aliphatic or

[1] *J. Amer. Chem. Soc.*, 1917, **39**, 2745; *J.*, 1918, 67A.

cyclic, and proteins (which he terms auxo-amylases) stimulate the
hydrolytic activity of saliva amylase, and probably also of pancreatic
amylase. L. Berezeller and E. Fodor [2] find that dilute solutions of
potassium permanganate, iodine, and hydrogen peroxide inhibit the
action of amylase, whereas formalin (probably due to the presence of
traces of formic acid) accelerates it. Yeast maltase, like zymase, is,
according to F. Schönfeld and H. Krumhaar,[3] an intracellular enzyme,
and can only be extracted after the yeast has been dried and the cells
ruptured. Its activity is stimulated by aeration, and may become
permanently weakened by prolonged absence of air, hence secondary
fermentation of malt beers is stimulated by introduction of air into
the beer. H. Euler has shown [4] that the formation of an enzyme
(invertase) in developing yeast is not necessarily parallel with the rate
of growth. Amino-acids stimulate this growth,· but not as much as
yeast water does. An interesting series of papers by M. Jacoby [5] on
the formation of the enzymes urease and catalase by bacteria has
appeared during 1917 and 1918, but the results are too specialised for
treatment here. H. v. Euler [6] shows that in the inversion of sucrose
by yeast the invertase increases to a maximum according to the equa-
tion $dx/dt = k(a - x)$, where a is the initial concentration of sucrose
and x is the amount inverted after time t. In the hydrolysis of starch
by *Mucor mucedo* the rate of the enzyme formation is constant, whilst
H. Colin and A. Chaudun [7] state that only with sugar concentrations
less than 2% does the inversion correspond to Wilhelmy's equation
$x = a(1 - e^{-kt})$. In a long paper O. Meyerhof [8] gives the results of his
researches on the kinetics of cell-free fermentation by zymase, and
emphasises the very important part which phosphates and hexose-
phosphates play therein. He confirms the stimulating effect produced
by the addition, up to certain limits, of hydrogen disodium phosphate,
and shows that the " induction period " observed, before fermentation
begins, when sugar is added to an extract of dried yeast, is lessened by
the addition of this phosphate to the sugar solution. He considers the
action is due to formation of hexose-phosphate. H. Euler and S.
Heintze,[9] investigating the esterification of hydrogen disodium phos-
phate when incubated with dried yeast and dextrose, show that the
maximum quantity of hexose-phosphate is formed when dried yeast

[2] *Biochem. Zeits.*, 1917, **84**, 42 ; *J.*, 1918, 133A.
[3] *Woch. Brau.*, 1917, **34**, 60, 157, 165, 180 ; *J.*, 1918, 161A.
[4] *Biochem. Zeits.*, 1918, **85**, 400 ; *J.*, 1918, 318A.
[5] *Biochem. Zeits.*, 1917, **79**, 35 ; **80**, 357 ; **81**, 332 ; **83**, 74; **84**, 354 and 358 ;
1918, **86**, 329 ; **87**, 129 ; **88**, 35 ; **89**, 350; *J.*, 1917, 663, 901, 1106 ; 1918, **386A**,
436A, 557A, 667A.
[6] *Z. Elektrochem.*, 1918, **24**, 173 ; *J.*, 1918, 524A.
[7] *Comptes rend.*, 1918, **167**, 208 ; *J.*, 1918, 525A.
[8] *Z. physiol. Chem.*, 1918, **102**, 185 ; *J.*, 1918, 711A.
[9] *Z. physiol. Chem.*, 1918, **102**, 252 ; *J.*, 1918, 711A.

containing 10–15% of moisture is used, and when the proportion of the yeast was large.

A valuable paper containing a summary of the present knowledge on proteoclastic enzymes and the results of extended research (especially on the autolysis of dried yeasts) was contributed by N. Ivanov.[10] His results show that the proteoclastic enzymes of yeast consist of protease (pepsin) and ereptase. K. G. Dernby [11] showed that tryptase was also present in yeast.

T. B. Robertson [12] and H. L. Holzberg [13] some years ago described a method for the purification of tryptase (trypsin) by precipitating it from its solutions by means of safranine. The safranine precipitate was proteoclastically active. J. T. Wood,[14] working on this subject, repeated this work, and from ordinary preparations of tryptase (Grübler's, Fairchild's. etc.) obtained similar results. But with preparations of his own which were fairly free from albuminous matter no precipitation was produced by safranine, the active enzyme remaining in solution. It appears that safranine precipitates the protein substance present in the usual tryptase preparations, which, in its turn, carries down the tryptase with it. If the precipitate (especially after drying) is washed with water the enzyme is gradually dissolved out again, the precipitate losing its activity. The protein is also partially redissolved. The process is thus useless as a means of purifying the enzyme. Wood, taking advantage of the fact that cellulose absorbs the impure mixture of protein and enzyme, and that after drying the colloidal (protein) portion adheres firmly to the paper, whereas the enzyme is very easily soluble, has evolved a method of purification which promises to be very valuable in enzyme research. He describes the method as follows : " Ordinary circles of Swedish filter paper (J. H. Munktell) 12½ cm. diameter, area 122 square cm., ash 0·00095 grm., averaging in weight 0·87 grm. air-dried, are soaked in the impure enzyme solution and dried quickly in a current of hot air. The average increase in weight is 0·054 grm. of added matter, or 0·41 mgrm. per square inch. When such paper is placed in water the enzyme dissolves quickly to a perfectly clear solution in a few minutes, whilst the colloidal matter with which it is associated adheres firmly to the paper. The solution is filtered after 15–20 minutes, by which time the whole of the enzyme matter is dissolved. If left for a longer time proteins begin to dissolve and the enzyme strength decreases." When the safranine solution is added to enzyme solution prepared in this way no precipitate is produced and the enzyme activity is not reduced.

O. Meyer [15] has recently discovered the co-enzyme of yeast, which

[10] *Biochem. J.*, 1918, **12**, 106 ; *J.*, 1918, **481A**.   For detailed abstract see also *J. Inst. Brewing*, 1918, **24**, 267.   [11] *J.*, 1917, 1023.
[12] *J. Biol. Chem.*, 1907, **2**, 317.   [13] *Ibid.*, 1913, **14**, 335.
[14] *J.*, 1918, 313T.   [15] *Z. physiol. Chem.*, 1918, **101**, 165.

previously had only been detected in yeast extracts, in the juice of muscles and of other tissues such as the liver. If yeast maceration juice, freed from the co-ferment by ultra-filtration, is treated with boiled muscle juice the fermenting power of the yeast juice is restored. Unboiled muscle juice does not possess this property owing to the presence in it of a substance which destroys the zymase. In his former work on the oxygen-respiration of yeast maceration juice the author showed that this juice contained the " enzyme " which is non-dialysable and thermo-labile, and the " respiration body " which is dialysable and thermo-stable. He now finds that the respiration of the " enzyme " portion of the yeast juice is restored by the addition of boiled muscle juice, as by that of boiled yeast juice. On the other hand the respiration of muscle tissue lost on extracting the muscle tissue with water is restored to the extracted tissue by the addition of boiled yeast juice as well as it is by that of boiled muscle juice. From his present work the author concludes that the co-enzyme of fermentation is, at least in part, identical with the respiration body of muscle tissue and of dead yeast, and thereby confirms the hypothesis that the earlier phases of respiration and fermentation are closely related.

H. Colin [16] has obtained a very active sucrase (invertase) solution by allowing a suspension of 25 grms. of yeast in 150 c.c. of water to putrefy till it was acid to litmus, but neutral to methyl orange and p-nitrophenol, then shaking the suspension with kieselguhr and filtering. A clear solution of very great activity is obtained capable of inverting 20 times its volume of 5% sucrose solution in an hour at 50° C. If shaken with a little toluene this solution will retain its activity for years. The same author and A. Chaudun [17] by varying the proportions of sucrase and sucrose in the hydrolysis of sucrose have obtained results confirming Brown's hypothesis of the formation of a compound between the sugar and the enzyme.

ANALYSIS.

Nagendra Chandra Nag and Panna Lal [18] describe " a simple and rapid method for the estimation of alcohol in spirituous liquors," for which they claim great accuracy and convenience. The method consists in treating a known quantity of the liquor in a glass tube graduated in tenths of a c.c. (or preferably finer) with an excess of anhydrous potassium carbonate, adding about 5–10% of water in case the percentage of alcohol is above 90. The mixture is then thoroughly shaken and allowed to settle (or preferably centrifuged), when it will separate into a lower layer of solid potassium carbonate, a middle layer of saturated potassium carbonate solution, and an upper layer of alcohol hydrate

[16] *Bull. Assoc. Chim. Sucr.*, 1918, **35**, 84; *J.*, 1919, 50A
[17] *Comptes rend.*, 1918, **167**, 338; *J.*, 1918, 600A.   [18] *J.*, 1918, 290T.

corresponding with the formula $4C_2H_5OH,H_2O$.   Each c.c. of the aqueous potassium carbonate contains 0·00275 c.c. of alcohol.   The alcohol hydrate has a specific gravity 0·8198 at 15·6° C. corresponding with 94·04% by volume, or 91·07% by weight of absolute alcohol.   The formula for calculating the percentage of alcohol by volume is :   Percentage=[V + $(v \times 0.00275)$] $\times$ [1–0·001068$(t$—15·6)] $\times$0·7936 $\times$94·06 $\div$ W, where V is vol. of alcohol hydrate in c.c., v vol. ot potassium carbonate solution, W the weight of the sample taken in grams, 0·00275 the solubility of alcohol in the carbonate solution, 0·001068 the apparent coefficient of expansion of the alcohol hydrate, 0·7936 the specific gravity of absolute alcohol at 15·6' C., and 94·06 the percentage of alcohol hydrate.   The tests can be made on 5 c.c. of liquor, and if v is less than 2 c.c. that correction may be disregarded.   The results agree within about 0·02% 'of those found by the distillation process. Solids in solution do not affect the result, and the process is equally applicable to methyl alcohol.

N. Schoorl and A. Regenbogen [19] have very carefully re-determined the densities of mixtures of ethyl alcohol and water at 15° C.   Carefully purified alcohol from various sources gave concordant values for specific gravity at 15° 1° C.=0·7936.   The densities of the mixtures from this alcohol differ appreciably from those of the Dutch official tables based on Baumhauer's determinations (1860), but agree very closely with those of Osborne and MacKelvey,[20] on which the U.S. Bureau of Standards tables are based.

Continuing his work referred to previously,[21] A. Reichard [22] finds the acid reaction to phenolphthalein in freshly harvested barleys much greater than (sometimes double) that to litmus.   During storage the former value gradually diminished and finally coincided with the latter. This is attributed to disappearance of amino-acids which are acid to phenolphthalein, but not to litmus.   This disappearance has been noted by Schjerning and others as characteristic of the " after-ripening " of barley, and the identity of the figures is a sign that the barley is thoroughly matured and fit for malting.   In view of the taking over in 1918 by the Government of large quantities of stored barleys from the brewers, a standard rapid method of taking the moisture of such barley was needed.   A Committeee of the Institute of Brewing devised such a method,[23] which is known as '' The Institute of Brewing method for the determination of the moisture content of barleys,'' and is now generally adopted in England.

For· the detection or determination of minute traces of oxalic acid

[19] *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20,** 831 ; *J* , 1918, 318ı.
[20] *J.,* 1913, 303.
[21] *Ann. Repts.,* 1917, **2,** 421.
[22] *Z. ges. Brauw.,* 1918, **41,** 57, 65, 75, 83, 89 ; *J.,* 1918, 523ᴀ.
[23] *J. Inst. Brewing,* 1918, **24,** 234 ; *J.,* 1918, 523ᴀ,

in beers, A. Bau [24] recommends precipitation as calcium oxalate by means of a reagent made by mixing 500 c.c. of 50% acetic acid containing 25 grms. of crystallised calcium chloride with 500 c.c. of saturated sodium acetate solution. ·The results with beers of various types ranged from 8 to 34 mgrms. of calcium oxalate per litre. The oxalic acid is mainly derived from the hops, but partly also from the malt.

U. Pratolongo [25] in a long paper gives the results of the investigation of 560 Italian wines examined for the purpose of arriving at a reliable means of discriminating between natural and adulterated wines, but finds that none of the rules based on the relation between alcohol content and acidity hitherto suggested is satisfactory. He proposes the division of Italian wines into two classes, " Normal " and " Abnormal," and gives tables for the former showing permissible acidity for various alcohol contents. For " abnormal " wines (comprising about 10% of the whole) he considers a " declaration of origin " as essential, and that all others which do not conform to the " normal " standards should be regarded as adulterated. In a later paper the same author [26] describes a method for determining the watering of wine based on the fact that a natural wine forms a saturated solution of potassium bitartrate and calcium tartrate. If a wine when treated with these two salts dissolves further quantities, the presence of watering is indicated.

G. de Astis,[27] in a long and very detailed paper, gives the result of a mass of work on the presence and determination of fixed organic acids, especially lactic acid, in Tuscan wines, and J. Laborde [28] gives elaborate particulars for the determination and separation of lactic, succinic, and malic acids in wines, but readers must be referred to the originals or the fairly full abstracts in our Journal.

For the detection of cider in wine P. Medinger and F. Michel [29] recommend the addition to 15 c.c. of the wine of a few c.c. of concentrated sodium nitrite solution. They state that pure wines give a bright yellow or yellowish-brown coloration, whereas if cider or perry is present a dark brown colour is produced and a brownish-black precipitate separates. F. Mach and M. Fischler,[30] testing this process on genuine wines from the Baden district, declare it to be insensitive, and that a definite result could not be obtained with less than 40% of cider. Certain genuine wines gave the dark reaction more markedly than cider.

[24] Woch. Brau., 1918, 35, 31, 40, 45, 51, 57, 63, 70 ; J., 1918, 524A.
[25] Staz. Sper. Agrar. Ital., 1917, 50, 315 ; J., 1918, 276A.
[26] Staz. Sper. Agrar. Ital., 1918, 51, 56 ; J., 1918, 745A.
[27] Annali Chim. Appl., 1918, 9, 155 ; J., 1918, 599A
[28] Comptes rend., 1917, 165, 793 ; J., 1918, 36A.
[29] Chem.-Zeit., 1918, 42, 230 ; J., 1918, 386A.
[30] Chem.-Zeit., 1918, 42, 326 ; J., 1918, 481A.

BREWING AND BREWING MATERIALS.

With the great shortage of cereals fit for human food, and of sugar, and with the consequent restriction of the use of these materials for brewing purposes, it was but natural that the quest for fresh brewing materials referred to in the report for 1917 should continue.

Sorghum vulgare or millet, a cereal of very wide geographical distribution, occurring in different countries in more or less distinct variations, and variously designated as millet, great millet, Sudan millet, d ura, durra, doura, Kaffir corn, broom corn, sorgho, and Guinea corn, has perhaps received the widest attention. Grown largely in France, Morocco, and Algeria, it has long been used as fodder, and the grain (both home-grown and imported) has been used to some extent by distillers in the same way as maize, but it has, recently also been tried, under stress of war conditions, by French brewers. From an important paper contributed by J. Raux [31] it is clear that the results there have, on the whole, been successful. Attempts to use the finely ground raw grain in the mash tun were unsatisfactory as the conversion of the starch was very imperfect and the filtration was much impaired. It is necessary to cook the millet, and this is best done by using coarsely crushed seed under pressure. The conversion is then easy, and the coarse fibre aids, instead of impairs, the filtration of the goods. Considerable quantities of the different varieties of sorghum have been imported into England, the amount in 1910 being over 20,000 tons. At the instigation of the Imperial Institute, which was able to put about 6 tons of Sudan dura at their disposal, L. Briant and H. Harman [32] have made very extended experiments with this material on a practical scale. The Sudan " Falerita " dura, which forms the staple article of food in the Sudan, grows to a height of 6–10 feet, flowers twice in the year, in May and October, and bears a large inflorescence carrying small round seeds about ⅛ inch in diameter. The testa is fairly hard and brittle, and the interior white and floury. Malting experiments gave a fairly tender malt showing good diastatic power and flavour, but the extract is extraordinarily low (about 30 lb. per quarter of 336 lb.). Roasted dura, both after malting and raw, gave good results as to flavour, colour, and extract as compared with roasted barley, though the advantage of malting before roasting was too slight to make malting worth while.

	Roasted after malting.	Roasted raw.	Roasted barley.
Extract per 336 lb.	83·5 lb.	87·0 lb.	80 lb.
Colour, 0·2% sol. in 1 in. cell (Lovibond)	25°	27°	30°

Practical porter brewings were made with the roasted raw dura

[31] *Brasserie et Malterie*, 1918, **7**, 372 ; *J.*, 1918, 317A.

[32] *J. Inst. Brewing*, 1918, **24**, 209 ; *J.*, 1918, 523A. See also *Bull. Imp. Inst.*, 1913, **11**, 33.

side by side with normal porter brewings, the only difference being that the 10% of roasted barley normally used in the grist was replaced by 7% of roasted dura. The porter brewed with the dura was better in colour than that with the barley, 'and the flavour, general characteristics, and palate fullness was in no way inferior.

Flaked dura was made on a practical scale with satisfactory results, the yield being 80% with 15% of meal as good cattle-food by-product. The flakes gave an extract of 91·5 lb. per 336 lb. Similar practical trials of making glucose were carried out with fairly satisfactory results, though the conversion was slow and difficult. The product was of the malto-dextrin type, and gave satisfactory results when used in the brewing of bitter and mild ales. The authors state : " We think, if sufficient quantity of dura is obtainable at a suitable price, it can be quite successfully employed in the manufacture of roasted grain as a substitute for roasted barley, as flakes, or as sugar of malto-dextrin type."

In connection with the use of raw cereals containing considerable quantities of oil and of proteins, it is necessary, however, to bear in mind the warning given by Driesbach, and referred to in a previous report,[33] as to the dangers to be guarded against, and to the liability of such materials to go musty on keeping if at all damp.

The Defren process,[34] which forms the subject of several U.S. patents, consists in subjecting suitable material containing starch and proteins to controlled conversion by acid and fermenting the wort obtained. Any materials containing starch and protein may be used, whether of cereal or other origin. The materials, either raw or subjected to partial caramelisation, are finely divided, mixed with acidulated water, and converted by heating under pressure at 152° C., the conversion being controlled by observations of the optical rotation and stopped at the desired point. The converted mixture is only neutralised to an acidity of 0·1–0·2%, so as not to coagulate the dissolved proteins, and may then be fermented direct, or a portion (say 10%) may be first concentrated, partially caramelised, and re-introduced into the main wort. Good flavour and palate fullness are claimed for the resulting beers, the types of which may be varied by controlling the conversions. H. Boulard [35] has taken out a patent on similar lines, using *Mucor Boulard* as the saccharifying agent, but the number and complicated nature of the stages of his process, and the introduction of a second ⋯ of vegetable culture, seem seriously to detract from the advantages claimed.

The number of papers on brewing technique in 1918 were not so

[33] *Ann. Repts.*, 1917, **2**, 434.
[34] *Western Brewer*, 1918, 50; *J. Inst. Brewing.* 1918, 191 and 282 ; see *J.*, 1917, 1059.
[35] Eng. Pat. 119833 ; *J.*, 1918, 779A,

numerous as those noticed in the Report for 1917, but the unpublished experiments were continued with satisfactory results. By careful selection of grists, attention to mashing heats, degree of attenuation, and general conditions, great improvement in flavour, and even in palate fullness, has been obtained over those beers of like gravity made in the early days of restriction, or in pre-war times. The greater use of the mash filter and the claim that by this means a softer palate flavour can be obtained should also be noted. Windisch, however, still maintains his view that a high proportion of alcohol as compared to residual matter is the most important cause of palate fullness.

An important paper on " A Belgian mashing system suitable for light beers " was read in May, 1918, before the Institute of Brewing, by G. M. Johnson.[36] Very briefly the process may be described as initial mashing at 100°–110° F., a " peptonisation " or " protein rest " at that temperature for 30–45 minutes (by which some of the proteins are degraded and made soluble), raising of the temperature by underlet liquor to 120°–125° F., a further short rest, and subsequent saccharification in stages at higher temperatures of about 158° and 165°, so as to get a dextrinous wort containing a large proportion of proteins. The author claims for light beers so made, full and pleasant flavour and good stability. The paper should be read by all operative brewers as it contains a great deal of suggestive matter which cannot be abstracted in the limited space of this report.

C. S. Ash [37] has published a more detailed account of his tannic acid process of rendering light beers more stable, referred to in a previous report.[38] H. F. E. Hulton [39] has described the process followed by himself and J. L. Baker for tracing infection in the brewery by not only forcing samples of the wort taken at all stages of brewing, but also by taking duplicates of the samples before pitching and infecting one of each set with a pure culture of yeast, before forcing it. H. Krumhaar [40] points out that when diluting war beers with unboiled waters containing considerable quantities of alkaline-earth carbonates, it is desirable to decarbonate such waters, especially if the character of the beer depends on lactic acid (see also Annual Reports, 1917, **2**, 427).

A Rippel [41] and H. Zikes [42] have both studied the effect of atmospheric pressure on the evolution of carbon dioxide during fermentation, and find that lessened pressure is accompanied by increased loss of gas. P. Petit [43] warns brewers not to neglect infection of worts with

[36] J. Inst. Brewing, 1918, **24**, 237 ; J., 1918, 778A.
[37] Western Brewer, 1918, **50**, 93 ; J. Inst. Brewing, 1918, **24**, 225.
[38] Ann. Repts., 1917, **2**, 436.
[39] J. Inst. Brewing, 1918, **24**, 258 ; J., 1918, 779A.
[40] Woch. Brau., 1918, **35**, 151 ; J., 1918, 779A.
[41] Centralbl. Bakt., 1917, ii, **47**, 225 ; J., 1918, 318A.
[42] Allg. Z. Bierbrau. u. Malzfabr., 1917, **38**, 229 ; J., 1918, 318A.
[43] Brasserie et Malterie, 1917, **7**, 273 ; J., 1918, 255A.

bact. termo, which frequently occurs in the summer from contact with unclean vessels or germ-laden air. Although the vigorous action of the yeast during fermentation destroys these bacteria, their action is often among the causes of trouble such as stench, haze, etc. P. Lindner [41] points out one cause of haze in thin beers as the presence of oxygen in some of the carbon dioxide used for carbonating. The oxygen stimulates the development of wild yeasts. In the same way in bottled beers, where the bottles are not completely filled, the air present may cause haze. [45] In German low-gravity beers " iron-sickness " has caused some trouble. This appears first as a greenish tint which gradually darkens and gives an inky appearance and taste to the beer. It is particularly troublesome in very thin beers, [46] some of the gravities apparently being as low as 1004°. The iron may sometimes be introduced in the diluting water, or may be taken up by these thin beers from contact with iron vessels, etc. The iron in the ferrous state first forms a colourless compound with the tannin, but this gradually becomes oxidised. In an acid beer colour does not develop, but in the very thin beers of very low acidity it does. Similar iron-sickness has been observed in wine, and in that case was cured by adding a little more tannin and thoroughly aerating. In this way the darker insoluble product was formed which gradually subsided, and the wine was finally clarified with gelatin. This treatment is less applicable with beers as they are generally carbonated before the malady appears. Windisch describes treatments applicable in some cases. But it is most important with beers of this low gravity to be particularly careful in ascertaining that the water used for diluting is absolutely free from iron, and that contact of the beer with iron is avoided. These results are also practically confirmed by F. Schönfeld. [47]

The red coloration sometimes produced when boiling wort with hops has been investigated by H. Krumhaar, [48] and also by A. Bau, [49] both of whom confirm the view generally held that it is caused by the action of calcium or magnesium bicarbonate or of sodium carbonate in the brewing liquor.

F. M. Maynard [50] has contributed a series of interesting articles on lager-beer brewing, and E. Schlichting [51] described before the U.S. Master Brewers' Association what he considers to be the best way of brewing the new regulation beers of less than $2\frac{3}{4}\%$ alcohol ($5 \cdot 6\%$ proof spirit) content.

[41] *Woch Brau.,* 1918, **35,** 225; *J.,* 1919, 87A.
[45] H. Will, *Z. ges. Brauw.,* 1917, **40,** 249; *J.,* 1918, 219A.
[46] W. Windisch, *Woch. Brau.,* 1918, **35,** 69, 95, 109, 153; *J.,* 1918, 779A
[47] *Z. ges. Brauw.,* 1918, **41,** 219; *J., Inst. Brewing,* 1919, **25,** 81.
[48] *Woch. Brau.,* 1918, **35,** 25; *J.,* 1918, 523A.
[49] *Ibid.,* 1918, **35,** 73, 79, 90; *J.,* 1918, 525A.
[50] *Brewers' J.,* 1918, 342, 382, 415; 1919, 34, etc.   [51] *J.,* 1918, 524A.

" Non-Alcoholic " Beverages.

In fermented beverages falling below the English excisable limit of 2% proof spirit --so-called " non-alcoholic beers " before the terms beer and ale were restricted by the Control Board to fermented malt liquors of over 1010 original gravity much work has been done and much improvement made. During the period of great shortage even of " war beers " these beverages found ready consumers, and some of them proved quite presentable products, though they lack the characteristic flavour and palate fullness of beers. An interesting report on this type of beverage issued by the Kentucky Agricultural Experimental Station[52] should be mentioned, as also A. Hadley's patent[53] for preparing such a beverage of original gravity 1016.

Yeast.

With the further lowering of the minimum original gravity of war beers the difficulty referred to in the 1917 Report of keeping up the quality of the yeast out-crop naturally became accentuated. To meet this to some extent the Excise allowed the brewing of a beer even above the maximum gravity and its subsequent breaking down with water or very light beer. The difficulty was also met on the lines indicated previously.[54] In this regard the work of F. Schönfeld and H. Krumhaar,[55] and of F. Schönfeld and M. Korn,[56] on the stimulation of maltase and zymase activity in yeasts by mono-potassium phosphate and other substances is of interest. F. Schönfeld and C. Goslich[57] record the diminution in size of the yeast cells grown in the very light German beers of about 1012 and under. T. Bokorny[58] in a paper on reproduction of yeast states that generally during fermentation, if the amount of yeast present is large, fermentation proceeds quickly and little sugar is assimilated, i.e. little fresh yeast is formed, and vice versâ. He therefore suggests that in fermenting the very light beers by employing a small quantity of pitching yeast slower fermentation would result with a larger development of fresh yeast. In some experiments he obtained fresh yeast to the amount of 16% of the weight of the sugar decomposed. L. Lindet[59] confirms Bokorny's results, and considers that fermenting power must be considered as a function of the plant power, as measured by the amount of sugar consumed by unit quantity of yeast for its plant life, and the zymase power as measured by the sugar consumed by unit quantity of yeast in accomplishing its zymatic function.

[52] Bull., 1915, 65; J., 1918, 276A.
[53] Eng. Pat. 113560; J., 1918, 220A.   [54] Ann. Repts., 1917, 2, 435.
[55] Woch. Brau., 1917, 84, 60, 157, 165, and 189; J., 1918, 161A.
[56] Ibid., 1918, 85, 129; J., 1918, 779A.
[57] Ibid., 1918, 85, 153; J., 1918, 779A.
[58] Ibid., 1917, 84, 269; J., 1918, 162A.
[59] Comptes rend., 1918, 166, 910; J., 1918, 436A.

A. Slator,[60] in an important paper, describes a method of measuring rates of growth of yeast by direct observation under the microscope at constant temperature. The generation times of individual cells growing in malt wort at 30° C. vary within limits which are 10 minutes on either side of the average time of 73 minutes. With old yeast introduced into a fresh wort no growth occurs for a time (lag-phase), and then the cells grow at the normal rate. Little or no lag occurs in yeast grown from spores. Oxygen is necessary for yeast growth, but the cells, in absence of dissolved oxygen, can utilise some of that chemically combined in the wort. Carbon dioxide inhibits growth.

H. W. Anderschou, W. Lambshead, W. Lambshead, jun., and J. M. Ramsay [61] claim to make brewers' yeast suitable for bakers by treating it first with a solution of borax and an alkali carbonate, and subsequently with a solution of alkali carbonate alone.

F. Boas [62] has studied the action of arsenic on yeast, but finds the toxic action vary very greatly according to conditions, an initial inhibition in a medium containing nitrogenous nutrient being sometimes transformed after some hours to a stimulating action.[63]

J. C. Drummond [64] has proved the presence of water-soluble vitamines in dried yeast and yeast extract (marmite), confirming A. Seidell.[65] Neither alcohol nor ether extracted this vitamine. No similar vitamine could be obtained from meat extract. The paper is a long and valuable one. This work further proves the great value of yeast as a food-stuff for man and animals. For human consumption the bitter constituents must be removed, but when it is mixed in their fodder animals take the simple dried yeast readily with exceedingly good results.

A. D. Emmet and L. H. McKim [66] obtained the same vitamine from an autolysed yeast filtrate by adsorption by Lloyd's reagent (a special form of fuller's earth), or by ordinary finely ground fuller's earth. K. Sugiura,[67] by extracting dried yeast with 5% salt solution and subjecting this extract in a collodion bag to air dialysis,[68] obtained the vitamine in crystalline form. The physiological activity of both of these products was demonstrated by their power of curing polyneuritis in pigeons. On the other hand it is curious to note that A. Harden and S. S. Zilva [69] failed to find the antineuritic or antiscorbutic vitamine in beer or malt.

[60] *Biochem. J.*, 1918, 12, 248; *J.*, 1918, 745A.
[61] Eng. Pat. 117666; *J.*, 1918, 600A.
[62] *Z. Gärungs-Physiol.*, 1917, 6, 1; *J.*, 1918, 218A.
[63] See also Harden and Young, *J.*, 1911, 705.
[64] *Biochem. J.*, 1917, 11, 255; *J.*, 1918, 134A.   [65] *J.*, 197, 562.
[66] *J. Biol. Chem.*, 1917, 32, 409; *J.*, 1918, 105A.
[67] *Ibid.*, 1918, 36, 191; *J.*, 1918, 748A.   [68] Kober, *J.*, 1917, 1038.
[69] *J. Inst. Brewing*, 1918, 24, 197; *J.*, 1918, 524A.

HOPS.

E. S. Salmon has continued his valuable researches on the cultivation of hops and the production of new varieties. His " Report on the Trial of New Varieties of Hops at East Malling Fruit Research Station, 1917," issued by the Wye Agricultural College, summarises much of his work up to the end of 1917, and is an important addition to our knowledge. He has also described [70] two varieties immune to mildew which he had reared as seedlings in 1914 amongst about seventy seedlings of wild hop from Italy. The remaihder of the seedlings were very susceptible to mildew. These two plants, one of which proved to be male and the other female, have developed well and maintained their immunity.

J. Schmidt,[71] continuing his researches on hops, in Carlsberg, has published three papers. The first relates to the distribution of the wild hop in Denmark. In the second he describes the result of cross-fertilisation between a female European hop plant and an American male plant. Although the American male plant has itself no aroma (the aroma being confined to the female plant), it can transmit the typical American aroma to the offspring of the cross-breeding. The investigations detailed in his third paper relate to the number of teeth in the margin of the hop leaf and show that, though this is to a considerable extent affected by environment, there are yet certain characteristics in this respect shown by the different clones.

An interesting discussion on the shortage of hops was held by the London Section of the Institute of Brewing[72] in June 1918, and in this relation it may be well to notice the claim put forward by G. H. Benjamin [73] that by careful drying of hops first at 120° F. for 1–3 hours, then at 140°–165° F. for 2–5 hours, and finally, if necessary, at 170° F. for $\frac{1}{2}$–1 hour, they may be got into a condition in which they may be stored indefinitely without deterioration.

Attention has been called [74] to Baker and Hulton's paper on dried hops, but in view of the importance of cattle feed at the present time, it may be advisable to give the chemical analysis of such dried hops. These authors found the average composition : Moisture 4·8%, ash 7·4%, matter soluble in ether (resins and trace of fat) 9%, proteins 22%, crude fibre 21·5%, pentosans 13%, and assimilable carbohydrates 35·3%. Calories per lb. 1062. Mixed with a material containing the necessary fat, dried hops should be a very valuable constituent of cattle food.

[70] *J. Agric. Sci.*, 1917, **8**, 455 ; *J. Inst. Brewing*, 1918, 32.

[71] *Comptes rend. Trav. Carlsberg*, 1917, **11**, 314 and 330 ; 1918, **14**, 1 ; *J. Inst. Brew.*, 1918, 275, 276.

[72] *J. Inst. Brewing*, 1918, 251.

[73] *Western Brewer*, 1917, **49**, 92 ; *J. Inst. Brewing*, 1918, 33.

[74] *Ann. Repts.*, 1917, **2**, 440.

BARLEY.

A very important monograph on " The Identification of Varieties of
Barley," by H. V. Harlan,[75] has been issued by the U.S. Department of
Agriculture, which, though primarily dealing with varieties grown in
America, is of great interest to the English brewer and maltster.

FUEL ECONOMY.

Early in 1918, owing to the heavy demands of our Allies on our coal
supplies, the brewing industry, in common with other industries and
with the private consumer, was called upon by the Government for
drastic reduction in its fuel consumption, a reduction of at least 25%
being indicated as necessary, and regular returns of coal consumption
at breweries was ordered. In September the Coal Controller said that
the reduction effected had only been about 10%, and concentration
of breweries was threatened unless this was largely increased. A special
meeting of the Institute of Brewing was called for October 7 [76] to discuss
the whole subject. At that meeting it was stated that the average
(reduced) consumption for August was 70 lb. of coal per bulk barrel
of beer brewed, whilst some brewers claimed to be working at a con-
sumption of 33 lb. per barrel.* A strong advisory " Committee of Fuel
Economy " was appointed by the meeting to work in conjunction
with the Coal Controller, and to help individual brewers in their
endeavours to economise, on which Committee the Coal Controller
was represented by his expert adviser, A. W. A. Chivers. This Com-
mittee got to work at once, and on October 18 issued a very valuable
" Memorandum," [77] containing detailed suggestions as to where and
how fuel economies could be effected in the brewery, and this memoran-
dum was sent to every brewer in the kingdom. A special meeting of
the Midland Counties Section of the Institute of Brewing was held [78]
on October 24, at which a valuable discussion on this subject took place,
and on December 9, at a meeting of the London Section of the Institute,
Mr. Chivers [79] gave a very able address on Coal " Economy," which again
was followed by a very valuable discussion. In the course of this
discussion L. C. Harvey called attention to the use in America of pulver-
ised coal for boiler furnaces, by which saving up to 35%, and even more,
is claimed. As a result of this action of the Institute of Brewing much
good work was done, and large economies in fuel consumption effected.

75 U.S. Dept. Agric., Bull. 622. For full abstract see J. Inst. Brewing, 1919,
31, or Brewers' J., 1918, 277, 310, 340.

76 J. Inst. Brewing, 1918, 24, 297.

* In connection with the great discrepancy of these figures, allowance must
be made for the character of the coal used. In the case of the brewery showing
the lowest figures high quality washed Welsh nuts were exclusively used, whereas
in breweries less favourably situated much lower quality coal had to be employed.

77 J. Inst. Brewing, 1918, 24, 289.   78 Ibid., 306.   79 Ibid., 1919, 25, 1.

A useful series of fourteen monthly articles on " Heat Economy " were contributed to the Brewers' Journal by F. M. Maynard[80] during 1917 and 1918.

Reference should also be made to the work of H. C. Porter and F. K. Ovitz[81] on the loss in value of coal by storage, and the remarks of G. C. Jones thereon.[82]

All these actions have been very helpful to brewers, and it has become apparent that in the majority of breweries the coal consumption per barrel of beer brewed was much higher than it should have been. Some of the economies effected have been of a temporary character, permissible only under war conditions of extra light beers for quick consumption, but many of them have been permanent, due to more efficient and scientific working, and these latter savings have sometimes been very large indeed. Thus, though the period of the war has been a time of stress and strain for the brewer, it has by compelling him to give a closer and more scientific study to his processes and modes of work put him in a position of much greater strength when more normal conditions return.

DISTILLING.

The distilling industry has played an important part during the war. Two organic solvents, alcohol and acetone, were absolute necessities in the manufacture of high explosives and other munitions. The usual sources of industrial alcohol soon proved entirely inadequate, but a large number of distilleries in the United Kingdom were making large quantities of alcohol in the form of whisky which only required distillation in the patent still to make silent spirit, from which alcohol of the necessary strength could be easily prepared. As a result whisky making was stopped, and all the output of alcohol from the distilleries was diverted to the Munitions Department. Next the supply from pre-war sources of the almost more important solvent acetone, proved equally inadequate. New plant was erected, but still more acetone was required, and the Munitions Department decided to start the Fernbach fermentation process as an auxiliary source of supply, and some of the distilleries were taken over and altered for the requirements of this process. It may be mentioned here that in 1915 C. Weizmann, of Manchester, isolated a more suitable ferment than that first used. This, which he termed By, is capable of attacking and fermenting substrates, such as maize or rice, and yielding a mixture of butyl alcohol and acetone in the relative proportions of 2 to 1. Output on a manufacturing scale had just commenced at the home distilleries

[80] Brewers' J., 1917, 343, 380, 418, 465, 500, and 1918, 33, 70, 111, 137, 178, 217, 245, 276, 312.
[81] U.S. Bur. Mines Bull. 136; J., 1918, 615A. [82] J., 1919,

converted for the purpose when the great shortage of maize necessitated
the abandonment of operations. In Canada a large distillery had also
been converted, and there very large quantities of acetone were success-
fully made, which greatly eased the situation. From a commercial
point of view this process could hardly become economically practicable,
unless uses could be found for the large quantities of butyl alcohol
simultaneously produced.

Though perhaps not strictly coming under the heading of distilling,
mention may be made here of the great advances which have recently
been made in the production of many organic acids by the fermentation
of solutions of various carbohydrates by specific ferments. Already
the production of lactic acid is commercially carried out in this way,
and experiments have shown the possibility of the similar production
of fumaric and citric acids. In the case of citric acid, where the demand
is very large and the cost of the natural product is very high, it is
almost certain that the fermentation method of production will become,
before long, a commercial process.

Here, as in the brewing industry, the normal raw materials consisted
largely of cereals suitable for human food, with the result that restriction
of their use took place. As a natural result distillers sought for new
substitutes, and a large number of the papers which have appeared
deal with trials with such substitutes. Amongst these substitutes were
low or waste molasses,[83] the vinasses therefrom being used as fertilisers ;
sotol,[84] a plant growing abundantly in Mexico and yielding 18–25
gallons of spirit per ton ; *Asphodel ramosus* (porazzo),[85] a tuberous
weed growing abundantly in Italy ; sizal[86] waste after the fibre has
been extracted. A number of trials to obtain alcohol by fermentation
from wood-pulp liquors and wood wastes have been made. The use
of moulds (*Mucor Boulard* etc.)[87] in the saccharifying of distillers'
mashes appears to have made a good deal of progress, and to be
practised in a number of distilleries.

A. Jonscher[88] has examined a number of French and German wine
distillates, and finds that the French are much nearer in composition
to the German than they were formerly.' Of 26 German cognacs
examined only 5 contained more than 100 mgrms. of higher alcohols
per 100 c.c., the remainder varying between 20 and 80. The French
cognacs used to contain 150–300 mgrms. of fusel oil per 100 c.c., but
now rarely exceed 80 mgrms.

[83] E. Galle, *Z. angew. Chem.*, 1918, **31**, 3 and 6 ; *J.*, 1918, 481A ; also H. C.
Brill and L. W. Thurlow, *Philippine J. Sci.*, 1917, **12A**, 267 ; *J.*, 1918, 318A.
[84] *U.S. Com. Rep.*, May 2, 1918 ; *J.*, 1918, 282R, 396R.
[85] *Annal. d'Ingegn. e d'Archit.*, April, 1918 ; *J.*, 1918, 263R.
[86] *Tropical Life*, 1917, **13**, 155 ; *J.*, 1918, 667A.
[87] U.S. Pat. 1266657 ; *J.*, 1918, 601 ; Eng. Pat. 102945 ; *J.*, 1918, 525A.
[88] *Z. öffentl. Chem.*, 1918, **24**, 25 ; *J.*, 1918, 345A.

Methyl Alcohol.

Methyl alcohol is now coming into great prominence as a valuable solvent in industrial processes, and attempts are being made to get permission for its unrestricted industrial use in the undenatured condition. A " Methyl Alcohol Committee " has been appointed[89] by the Association of British Chemical Manufacturers, and one of the arguments brought forward in proof that denaturing is not necessary is the fact of its known toxicity, which would itself prevent any tendency for illicit drinking. A valuable paper on the importance of the industrial uses of methyl and a review of the published data as to its toxicity was given by T. D. Morson.[90] Details of six fatal cases of poisoning by methyl alcohol were also given by A. O. Gettler and A. V. St. George.[91] In his paper Morson points out the great importance of methyl alcohol in chemical manufactures, instancing especially the manufacture of dyestuffs, medicinal chemicals, formaldehyde, and photographic chemicals, and claims for it the right to be considered a " key " chemical. He quotes from the report of the Departmental Committee on Industrial Alcohol (1905) the statement : " Methyl alcohol does not fall within the charge to spirit duty in Germany and may be used freely for industrial purposes without control by the revenue authorities." Its classification by the Customs and Excise as " plain spirits " and consequent subjection to the same rates of duty as ethyl alcohol could only be justified by the assumption that it was potable, and the proofs of its absolute toxicity render its retention as an excisable article absolutely unjustifiable.

WINES.

Much of the work on wines published in 1918 was in connection with detecting adulteration, and has been referred to already (p. 408). C. Mensio[92] has experimented on the use of preparations of sulphur dioxide, some containing also phosphoric acid and ammonia, during the making of wine in order to neutralise the harmful effect of grapes damaged by mould etc, amongst those being used. He found that the use of sulphur dioxide in any form was advantageous, the wines being brighter, that the best form in which to use it seemed to be as metabisulphite, and that the addition of phosphoric acid and ammonia was unnecessary. F. A. Sannino[93] found that calcium sulphite may be substituted for potassium metabisulphite, which, owing to the potash famine, was so difficult to obtain during the war. By the so-called " plastering " of wines (*i.e.* the addition of calcium sulphate to the

[89] *J.*, 1918, 257R.   [90] *J.*, 1918, 26T.
[91] *Amer. J. Pharm.*, 1918, **90**, 280 ; *J.*, 1918, 318A.
[92] *Staz. Sperim. Agrar. Ital.*, 1917, **50**, 300 ; *J.*, 1918, 102A.
[93] *Revista Viticolt.*, 1917, **23**, 330 ; *J.*, 1918, 103A.

must to precipitate some of the organic acids, and so prevent the tendency to turbidity on keeping or rise in temperature) slight increase of acidity is produced. Chancel's view of this reaction, $2C_4H_5KO_6 + CaSO_4 = C_4H_4CaO_6 + C_4H_6O_6 + K_2SO_4$, is generally accepted. A. Borntraeger [94] has carried on practical experiments in three successive years with white Catalanesca grapes both with and without addition of pure calcium sulphate. In all cases the acidity was slightly increased in the plastered wine, but not to the full extent indicated by the equation as calculated by the amount of sulphate present. He considers, however, that the discrepancy was due, in part at least, to the presence of unaltered calcium sulphate, and suggests other contributory causes. J. Laborde [95] has carried out researches on the fixed acids in wine. In sound red and white wines he has found the following acids, the quantities given being grms. per litre : lactic acid 1·06–1·95, succinic acid 0·61–0·75, malic acid 0·45–2·86, and tartaric acid 1·66–2·88. In two Algerian wines citric acid was found to the extent of 1 and 1·5 grms., but the author considers that this had probably been added. In sick wines the fixed acidity was generally reduced and the volatile acidity increased. G. de Astis [96] in a long and interesting paper gives the results of the examination of a large number of Tuscan wines in the same direction. He finds the total fixed and volatile acids as equivalent to 1·8–4·2 grms. of tartaric acid acidity per litre, whilst of these the lactic acid is equivalent to 0·45–1·7, the succinic to 1·0–1·7, and the volatile acids to 0·7–1·8. The proportion of lactic acid is generally high in new Tuscan wines. W. l. Baragiola [97] points out that the addition of potassium tartrate to wines to reduce the acidity [98] may alter the relation between the quantities of total tartaric acid and non-volatile acids present in normal wines, and so render impossible the detection of added water.

E. Kayser [99] considers that the disease of " bitterness " in wine is due to the reduction in the fixed acids and total tartaric acid, but not of the volatile acids and the production of more esters, especially butyric ester ; and he also finds an increase in the amount of ammonia. Investigating the malady of " white casse," D. Moreau and B. Vinet [100] conclude that it is brought about by the presence of iron and phosphoric acid. Free tartaric acid favours the disease, de-acidified wines being generally immune. The malady may be prevented by the addition of 1 grm. (in some cases by 0·5 grm.) of citric acid per litre, or by

[94] *Giorn. Viticolo Ital.*, 1917, 412 ; *J.*, 1918, 102A.

[95] *Comptes rend.*, 1917, **165**, 793, 1017 ; *Ann. Chim. Analyt.*, 1918, **23**, 127 ; *J.*, 1918, 36A, 68A, 481A.

[96] *Annali Chim. Appl.*, 1918, **9**, 155 ; *J.*, 1918, 599A.

[97] Schweiz. Ver. anal. Chem., May, 1918 ; *J.*, 1918, 779A.

[98] See Paul, *Ann. Repts.*, 1917, **2**, 443.

[99] *Rev. Viticult.*, 1917, **47**, 70 ; *J.*, 1918, 68A.

[100] *Bull. Soc. Agric. France*, 1917, 267, 292 ; *J.*, 1918, 189A.

treating " green " wines with de-acidifying agents. The presence of tannin perceptibly aggravates the disease, producing a bluish colour.

Bandna Must.

A must obtained by extracting the banana (both pulp and skin) was found by R. Perratti and V. Riviera [101] to contain four organisms : a *Sacch. musae*, a variety of *Oospora lactis*, a *Mycoderma*, and a special bacterium. On fermentation of this must a slightly alcoholic liquid was obtained of good colour, and of attractive character, with the agreeable aroma of the fruit.

VINEGAR.

C. A. Mitchell [102] points out that the origin generally given in the textbooks of the trade numbers 16, 18, 20, 22, and 24, by which vinegars are sold (*i.e.* that they indicate the strength of the vinegar), is incorrect. The true origin appears to be that they originally referred to the price per gallon at which they were sold, and not to their acetic strength, and that in fact the same number of different makes varied in strength. Thus No. 16 vinegar sold by different makers varies between 3·5 and 5%, and No. 24 between 5·2 and 6%.

There is one interesting effect of war conditions on the vinegar industry which deserves mention. Owing to the recent great restriction in the use of the cereals used in the production of vinegar the quantity made was much below the demand, and the vinegar was sent into the trade new, instead of being stored for some time to clarify. As a result it still contained bacteria which, when it was kept in a warm place, destroyed some of the acetic acid, and consequently of its strength, causing complaints that the right strength had not been supplied.

[101] *Staz. Sperim. Agrar. Ital.*, 1917, **50**, 433 ; *J.*, 1918, 524A.
[102] *J.*, 1918, 148R.

FERMENTATION INDUSTRIES—1919.

By Adam Tait and Louis Fletcher,

Chemists, Messrs. Wm. Younger and Co., Ltd., Brewers, Edinburgh.

Treating the subject of fermentation generally there are no startling discoveries to record during the period under review. The production of glycerol by fermentation methods is perhaps the most striking feature. This, however, can hardly be viewed in the light of a discovery, but credit must be given for the adaptation of the process to war needs and for the modifications which have produced such excellent results.
It is noteworthy that much has been published relating to the utilisation of by-products and waste in different branches of the fermentation industry. The need for avoidance of loss was strongly emphasised during the war, and the experience gained during that time ought to lead to the application of similar ideas to purely peace-time industries.

With regard to brewing, the restrictions enforced during the war have recently been relaxed to the extent that brewers are now allowed unrestricted output provided the *average* gravity of the beer does not exceed 1044 for home consumption -with the customary special concessions to Ireland.

In concluding this short introduction the reviewers wish to record their indebtedness to Mr. J. S. Ford, who has made many suggestions which have been of great assistance in the compilation of the report.

Chemistry.

As was found to be the case in other years, the bulk of the work falling under this heading has been in connection with enzymes. The writers have mainly selected the investigations closely concerned with the fermentation industries, but it was thought expedient to deal briefly with a few instances where a consideration might help to a better understanding of the enzymes in question.

General enzymes.

H. Maggi [1] has attempted to demonstrate the relationship between amylase, peroxydase, and catalase. He refers to Woker [2] who attri-

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[1] *Helv. Chim. Acta*, 1918, 1, 433; *J.*, 1919, 25A.   [2] *Ber.*, 1917, 50, 679.

butes the simultaneous presence of catalase and peroxydase in many enzymes to the presence of an aldehyde group, which unites with hydrogen peroxide to form a secondary peroxide. Maggi therefore considers the possibility of the aldehyde group being capable of exerting diastatic action, and to prove his theory he studied the action of formaldehyde on starch by the capillarity method. He considers his results to show that the behaviour of formaldehyde towards starch closely resembles that of amylase. In connection with the supposed amyloclastic property,of formaldehyde H. Sallinger [3] has performed a series of experiments. He digested a solution of amylo-dextrin (Lintner) with formaldehyde for 44 hours at 37° C., and found no change during that time in the optical activity of the solution, thus confirming Kaufmann's [4] previous observation. Further he treated a solution of soluble starch (Wolff-Fernbach) with formaldehyde. He removed the latter as completely as possible and found only a slight reducing power towards Fehling's solution, attributable to residual traces of formaldehyde. Taken in conjunction with some other work this author concludes that formaldehyde is enzymatically indifferent towards starch. J. Wohlgemuth [5] has been unable to confirm the experimental results of Woker already referred to. The severe criticisms of the latter author's work advanced by Kaufmann [6] are supported. He further shows that formaldehyde forms a loose combination with starch, the iodine-reacting group of the latter being fixed so that a starch-iodide reaction no longer occurs. If the formaldehyde is removed from solution it is found that the starch can be recovered unchanged in amount and in its properties. W. von Kauffmann and A. Lewite [7] again refute Woker's interpretations of his observed facts, and advance similar ideas to Wohlgemuth in explanation thereof. In the same paper the authors contribute some information regarding the colours of iodine solutions.

According to H. von Euler and R. Blix,[8] the catalase action in yeast cells can be increased by the addition of protoplasmic poisons such as toluene, or by dehydration provided the enzymes are not destroyed. Maltase is an intracellular enzyme,[9] and diffusion from the yeast cell can only take place when the cells have been killed or ruptured, although F. Schönfeld, H. Krumhaar, and M. Korn [10] found that killing by means of toluene did not enable the maltase to escape from every kind of yeast. These authors also state that maltase activity of yeast from weak wort is lower than that of yeast from wort of normal gravity.

[3] Ber., 1919, 52, 651; J., 1919, 433A.   [4] Ber., 1917, 50, 198.
[5] Biochem. Zeits., 1919, 94, 213; J. Chem. Soc., 1919, i, 361.
[6] Ber., 1917, 50, 198.
[7] Ber., 1919, 52, 616; J. Inst. Brew., 1919, 25, 373.
[8] Z. physiol. Chem., 1919, 105, 83.   [9] Cp. Ann. Repts., 1918,
[10] Woch. Brau., 1918, 35, 181; J., 1919, 155A,

H. von Euler and O. Svanberg [11] have studied the fermentation of sugars in alkaline medium ($P_H^+=8$). Dextrose, lævulose, sucrose, and invert sugar are rapidly fermented, mannose and galactose are not so readily attacked, while maltose is unaffected. It is concluded that maltase is inactive at P_H^+ 8. These authors have also studied the influence of a large number of cell poisons on the fermentation of sugars in alkaline medium. The influence of hydrogen-ion concentration on the enzymic activities of three typical amylases is the subject of a paper by H. C. Sherman, A. W. Thomas, and M. E. Baldwin. [12] The results confirm these of Sherman and Thomas [13] for the optimum hydrogen-ion concentration of malt amylase. In their experiments the authors used suitable phosphate media for controlling the hydrogen-ion concentration. Their figures for the upper and lower limiting values and for the optimum values are :

	Limits	Optima
Pancreatic amylase.	4–10	7
Malt amylase	2·5 - 9	4·4–4·5
Aspergillus oryzæ amylase . . .	2·6 8	4·8

The writers of this report have found that at 18° C. the optimum for malt amylase is P_H^+ 5, with limiting values of 2·3–8·9.

In connection with the enzymes of *Aspergillus oryzæ* G. Kita [14] has investigated the influence of calcium salts. He finds the action of the liquefying enzyme is accelerated at 25° C. and at 50° C. by small additions of calcium sulphate or chloride, even in cases where the saccharifying enzyme is retarded.

In similar experiments using malt amylase both enzymes were interfered with at the low temperature, but at 50° C. the liquefying enzyme was accelerated. The author's conclusion is that where liquefying and saccharifying actions proceed simultaneously, as in Japanese brewing and the " amylo " process, the addition of calcium salts is an advantage as it helps the attack on refractory particles of starch whilst · the retarding influence on saccharification is of no importance. Some interesting work has been published by H. Colin and A. Chaudun, [15] dealing with the law of sucrase action. The results are in accordance with A. J. Brown's [16] hypothesis that an intermediate compound of sucrase and sucrose is formed which decomposes into sucrase, dextrose, and lævulose. Later the same authors, continuing their work on sucrase action, [17] find that, for a given concentration of enzyme and the initial concentrations of sucrose increased sufficiently, there is a falling·

[11] *Z. physiol. Chem.*, 1919, **105**, 187 , *J.*, 1919, 734A.
[12] *J. Amer. Chem. Soc.*, 1919, **41**, 231 ; *J.*, 1919, 229A.   [13] *J.*, 1915, 371.
[14] *Mem. Coll. Eng. Kyoto Imp. Univ.*, 1918, **2**, 1 ; *J.*, 1919, 508A.
[15] *Comptes rend.*, 1918, **167**, 208, 339 ; *J.*, 1919, 550A.
[16] *Chem. Soc. Trans.*, 1902, **81**, 388.
[17] *Comptes rend.*, 1919, **168**, 1274 ; *J.*, 1919, 550A,

off in the initial rate of hydrolysis. They consider that this is related to the viscosity of the solutions and that in fact, when the sucrose is in excess of the sucrase, the velocity of hydrolysis is proportional to the fluidity of the solution, or $V = \alpha F$, where V = the velocity of hydrolysis measured by change of rotation of the solution in a given period from the start, F the fluidity (inverse of viscosity) measured with an Ostwald viscosimeter, and a a constant which is proportional to the concentration of sucrase.

Yeast enzymes.

The importance of the hydrogen-ion concentration when dealing with the various functions of enzymes is gradually becoming more and more recognised. Sörensen's classical work [18] on the subject did much to pave the way for other workers, besides instituting reliable methods well adapted to the peculiar requirements of this application of electro-motive force.

In this connection H. von Euler and F. Emberg[19] have studied the influence of varying the hydrogen-ion concentration on the fermentative power, inverting power, and maltase activity of a bottom fermentation yeast. They have plotted curves, using as ordinates the fermentative power of the yeast and as abscissæ values of P_H^+ ranging from P_H^+ 2 on the acid side to P_H^+ 8 on the alkaline side. These curves show that the fermentative power falls away much more quickly in presence of hydroxyl-ions than in presence of increasing amounts of hydrions. The writers of this report have assisted in work of a similar nature dealing with the action of malt amylase on soluble starch solutions adjusted to varying P_H^+ values by the addition of suitable phosphates, and in their work the same general principle was observed. Euler and Emberg further state that sucrase in the living cell is affected in exactly the same way as the enzyme in the free state. The maltase activity of the living yeast cell was found to be completely inhibited by a very small concentration of hydroxyl-ions ($P_H^+ = 8$). Further experiments on the same lines were carried out, first of all submitting the yeast to a treatment with liquids having hydrogen-ion or hydroxyl-ion concentrations ranging from $P_H^+ = 3.5 – 3.8$ to $P_H^+ = 6.6 – 7.2$. Such treatment influenced the enzymic activities of the yeast, including the synthetic processes concerned in the growth of the cell.

Reproduction and composition of cells were influenced in a pronounced degree. H. Euler, O. Svanberg, and S. Heintze [20] state that at 16° C. an increase in P_H^+ from the optimum for yeast sucrase (4·67 to 5·07) to 7·7 reduces the activity of the sucrase from 0·067 to 0·007. A practical suggestion is put forward by F. Schönfeld, H. Krumhaar,

[18] *Comptes rend. Trav. Lab. Carlsberg*, 1909, **8**, 1.
[19] *Zeits. f. Biol.*, 1919, **69**, 349; *Woch. Brau.*, 1919, **36**, 166.
[20] *Fermentforsch.*, 1918, **2**, 194; *Chem. Zentr.*, 1918, ii, 746.

and M. Korn,[21] who have observed that the maltase activity of yeast is greatest when the fermentation is at its maximum. They suggest that yeast removed at this stage might be added to cleansed beer since it possesses greater maltase and zymase activities than yeast which normally remains in beer when leaving the tuns.

The effect of various antiseptics on the enzymic activities of yeast has been studied by T. Bokorny,[22] who finds that 0·2% formaldehyde renders the yeast quite inactive ; at a concentration of 0·1% the zymase is destroyed in two days whereas the sucrase activity is not destroyed within this period even with a 1·0% concentration. It is thus possible with the aid of formaldehyde to prepare a yeast which will invert, but not ferment, sugar. Mercuric chloride of 0·1% strength suppresses the zymase without preventing sucrase action. By treatment with phenylhydrazine a yeast can be obtained which will ferment dextrose, but not maltose. In presence of 10-20% alcohol the fermentation of sucrose is very slight, although the zymase is not permanently destroyed. Absolute alcohol does not render sucrase inactive within 20 days, but it destroys the zymase activity in 10 minutes. H. Zikes,[23] experimenting with six varieties of bottom-fermentation yeasts, shows that all become adapted to the temperature at which they are grown. Those kept at 8° C. grew more rapidly up to 20° C. than those kept at 25° C., and these latter grew much better at high temperatures than the cold-stored yeasts.

The products of the autolysis of both bottom and top fermentation yeasts were isolated by J. Meisenheimer,[24] who found glycine, alanine, valine, leucine, proline, phenyl-alanine, aspartic acid, glutaminic acid, tyrosine, and tryptophane. Serine and cystine were recognised with less certainty, and it is believed that amino-butyric acid was present. Glucosamine was detected in the cell residue.

Fermentation.

O. Meyerhof [25] has described some work relating to the kinetics of cell-free fermentation by zymase. The addition of sugar to an extract of dried yeast containing zymase, but free from cells, is succeeded by a period of quiescence during which no sign of fermentation is observable. This interval, called by Lebedeff the "induction period," is shorter with sucrose than with dextrose or laevulose ; it can be shortened by previously warming the sugar solution with di-sodium hydrogen phosphate, or by grinding the dried yeast with glass powder. The

[21] Woch. Brau., 1918, **35**, 175 ; J., 1919, 87A,.
[22] Allgem. Brau- u. Hopfenzeit., 1918, **58**, 1093 ; J. Inst. Brew.,1919, **25**, 314.
[23] Allgem. Zeits. Bierbrau. u. Malzfabr., 1918, **46**, 359 ; J. Inst. Brew., 1919, **25**, 315.
[24] Z. physiol. Chem., 1919, **104**, 229 ; J., 1919, 475A.
[25] Z. physiol. Chem., 1918, **102**, 185 ; J. Inst. Brew., 1919, **25**, 211.

presence of a small amount of hexose-phosphate abolishes the induction period. After the induction period the fermentation of sugar by maceration juice always begins with a strong acceleration due to the phosphate in the juice. Increasing the amount of phosphate reduces the rate at which the velocity of the fermentation increases, but the maximum velocity eventually attained is higher than in the absence of free phosphate, until a certain maximum amount of the free phosphate is reached; further addition of phosphate then reduces the maximum velocity attainable. Other salts such as sodium chloride also reduce acceleration, and it is concluded that phosphate in addition to its specific accelerating effect on fermentation has a general salt function by which it inhibits fermentation. Reference should be made to Harden and Young,[26] who have published a good deal of work on the subject.

The rôle of phosphates in alcoholic fermentation is discussed by H. Euler and S. Heintze,[27] who consider that the esterification of phosphoric acid by dried yeast in the presence of a protoplasmic poison, such as phenol, is related to the amount of water remaining in the yeast after the drying process. The maximum esterification is observed when dried yeasts containing from 10 to 15% of moisture are employed. Increasing the quantity of yeast used in individual experiments appears to occasion a much greater increase in the amount of hexose-phosphate produced. In using beet molasses and sugar for yeast manufacture it is necessary to supplement the phosphoric acid present, which amounts to about 0·06% in molasses (x. Ellrodt[28] states that superphosphate has been used for this purpose, and he gives details for its use and also a table showing the amounts of superphosphate required per 100 kilos of molasses, to obtain given yields of yeast.

The question of the aldehyde stage in alcoholic fermentation has been investigated by C. Neuberg and E. Reinfurth.[29] After discussing the previous work on the presence of pyruvic acid and acetaldehyde as intermediate products in alcoholic fermentation, the authors show that in presence of a secondary sulphite (neutral sodium sulphite) the acetaldehyde formed in the alcoholic fermentation of sugar can be accumulated to the amount of 73·45% of that required by theory, a result which they claim as proving that acetaldehyde does constitute a stage in the fermentation process. How far the authors are justified in drawing these conclusions from such abnormal fermentations, the present writers leave those who have studied the subject of fermentation to judge.

[26] J. Inst. Brew., 1908, 14, 547; 1909, 15, 626; 1910, 16, 569.

[27] Z. physiol. Chem., 1918, 102, 252; J. Chem. Soc., 1919, i. 58.

[28] Brennereizeit., 1919, 36, 8239; J., 1919, 785A.

[29] Biochem. Zeits., 1918, 89, 365; J. Inst. Brew., 1919, 25, 181. See also J. Inst. Brew., 1911, 17, 392, 520, 700; 1912, 18, 48; 1913, 19, 233, 382, 469; 1914, 20, 127, 428.

A. Oelsner and A. Koch [30] have failed to confirm the statements of Wilenko [31] that the course of the fermentation of sugar in an alkaline phosphate medium is changed and that no carbon dioxide is formed under these conditions. The alkalinity delays the fermentation, but alcohol and carbon dioxide are always obtained. The observation of Neuberg and Färber [32] that more aldehyde is produced when the fermentation is conducted in an alkaline medium is confirmed.

For the production of fumaric acid in the fermentation of sugar by *Aspergillus fumaricus* C. Wehmer [33] gives the necessary conditions and details some actual results. The optimum temperature for the growth of the organism is 22° C. and the maximum about 30° C. Oxygen is a necessary factor, and for continuous fermentation, calcium carbonate. Thus 20 grms. of sugar in 20% solution and 2·87 grms. (dry weight) of *Aspergillus fumaricus* dissolve 15 grms. of calcium carbonate and produce 33 grms. of calcium salts, consisting chiefly of the sparingly soluble normal fumarate, but containing also varying quantities of the easily soluble hydrogen fumarate, about 4% calcium citrate, and the calcium salt of another, unidentified acid. The sugar is completely fermented and 60 70% converted into acids. The formation of fumaric acid during the fermentation of sugar was previously noted by F. Ehrlich, [34] but it appears that this worker used *Rhizopus nigricans* for his fermentations, and his claim [35] is promptly followed by a reply from C. Wehmer, [36] who denies that *Rhizopus nigricans* produces fumaric acid.

Starch.

1919 has been an exceedingly lean year as regards contributions to our knowledge of the starch question. It may be that much data is being accumulated, or on the other hand its very complexity has caused a temporary abandonment of the problem. The writers are of opinion that little real progress in the elucidation of the starch problem is likely to be made until new methods of attack are developed.

H. C. Sherman, F. Walker, and M. Caldwell [37] have examined the action of enzymes on starches of different origin. When purified by washing with very dilute sodium hydroxide, wheat, rice, and maize starches are hydrolysable at the same rate by the same kind of amylase, and this is true for a large variety of agents, such as saliva, pancreatin, purified pancreatic amylase, malt extract, purified malt amylase, taka-diastase, or the purified amylase of *Aspergillus oryzæ*. These results

[30] *Z. physiol. Chem.*, 1919, **104**, 175; *J.*, 1919, 382A.

[31] *Z. physiol. Chem.*, 1917, **100**, 255; *J.*, 1917, 1283.

[32] *Biochem. Zeits.*, 1916, **78**, 238.

[33] *Ber.*, 1918, **51**, 1663; *J.*, 1919, 50A.   [34] *Ber.*, 1911, **44** 3737.

[35] *Ber.*, 1919, **52**, 63; *J.*, 1919, 300A.

[36] *Ber.*, 1919, **52**, 562; *J.*, 1919, 509A.

[37] *J. Amer. Chem. Soc.*, 1919, **41**, 1123; *J.*, 1919, 651A.

confirm those of J. S. Ford and J. M. Guthrie.[38] Potato starch, washed with water, showed in general an enzymic hydrolysis equal to or slightly greater than the cereal starches. The authors, who state that potato starch washed with water only, is almost pure, must be considered fortunate in their supply of this material, for it has been the writers' experience that an extensive treatment is necessary before potato starch is obtained sufficiently pure for enzyme work. A rather important paper has been published by J. Small[39] in which he introduces a new method for the preparation of soluble starch. The merit of this work is that the author has been able to obtain a product of 100% soluble starch as against a product by Lintner's method of 95% soluble starch. 2–20 grms. of potato starch is heated with 100 c.c. of re-distilled 95% alcohol containing 0·75 c.c. of hydrochloric acid (sp. gr. 1·19) in a boiling water-bath under a reflux condenser, the mixture being shaken vigorously from time to time. After the alcoholic liquid has been boiling for ten minutes the alcohol is filtered off as quickly as possible, and the residue washed with distilled water until free from acid. If the proportion of potato starch is increased, Small found that some insoluble starch remains even after fifteen minutes' boiling. With larger quantities of acid a certain amount of hydrolysis takes place, which is in direct proportion to the concentration of the hydrogen-ions. A. Leulier[40] describes a similar method of preparing soluble starch, only in place of hydrochloric acid he uses sulphuric acid.

ANALYSIS.

Alcohol.

K. Hoepner[41] has introduced a method for the determination of ethyl alcohol, aldehyde, and acetone in mixtures of the same. Finding that acetone is not oxidised by chromic acid, he distils it from the oxidised mixture and estimates its amount by forming a ketoxime with hydroxylamine hydrochloride. In another portion treated with hydroxylamine hydrochloride the aldehyde and acetone form aldoxime and ketoxime respectively, and their measure is obtained by the equivalent quantity of hydrochloric acid liberated. Alcohol and aldehyde are determined together in a third portion by chromic acid oxidation. After deducting the chromic acid equivalent of the aldehyde, the remainder of the quantity reduced is a measure of the alcohol present.

The oxidation of ethyl alcohol by means of potassium permanganate is the subject of a long paper by W. L. Evans and J. E. Day,[42] wherein

[38] *J.*, 1905, 605.
[39] *J. Amer. Chem. Soc.*, 1919, **41**, 113; *J. Inst. Brew.*, 1919, **25**, 180.
[40] *J. Pharm. Chim.*, 1918 (vii.), **18**, 291; *J.*, 1919, 86A.
[41] *Z. Unters. Nahr. Genussm.*, 1917, **34**, 453; *J.*, 1919, 735A.
[42] *J. Amer. Chem. Soc.*, 1919, **41**, 1267; *J.*, 1919, 793A.

they describe a series of elaborate experiments designed to elucidate the following points :—(1) The nature of the products formed when ethyl alcohol is oxidised by neutral or alkaline permanganate at different temperatures ; (2) the effect of changing the temperature and altering the initial concentration of alkali, and the combined effect of varying these factors ; (3) the mechanism of the oxidation.

For the detection of methyl alcohol in ethyl alcohol E. Salkowski [43] brings forward a test depending on the oxidation of the impurity and the recognition of the resulting formaldehyde. For the test the alcohol is diluted with nine times its volume of water. 0·5 c.c. of the diluted mixture is treated with 3 c.c. of dilute sulphuric acid and 3 c.c. of 1% potassium permanganate solution. After eight minutes the solution is decolorised with a saturated solution of oxalic acid and then distilled. The distillate is heated to boiling with the addition of 0·08 grm. of peptone, 3 drops of 3% ferric chloride solution, and its own volume of hydrochloric acid (sp. gr. 1·19). As little as 1% of methyl alcohol in the original gives a bright violet coloration. The author rightly points out that this and other tests based on the formation and recognition of formaldehyde are reliable only in the absence of the higher alcohols which would yield products giving a similar reaction under these oxidation conditions. In testing for methyl alcohol in ethyl alcohol H. Wolff [44] used apomorphine which with formaldehyde gives a blue-violet coloration, whilst ethyl, propyl, and amyl alcohols yield products giving a yellow or red-brown coloration. J. W. Ehman [45] doubts the trustworthiness under certain conditions, notably temperature, of the U.S. Pharmacopœia test for methyl alcohol in ethyl alcohol and recommends precautions which obviate errors from that source.

F. W. Babington and A. Tingle [46] describe a method for the determination of small amounts of benzene in ethyl alcohol.

C. E. Davis and M. T. Harvey [47] have determined the freezing-point curves and densities of denatured alcohol-water mixtures.

Starch.

" The quantitative estimation of soluble starch in presence of starch and its hydrolytic cleavage products " is the title of a paper by J. C. Small,[48] and the method is of some importance inasmuch as up to the present there has been no known method for the quantitative separation of soluble starch from the higher dextrins. The compound of iodine and soluble starch is insoluble in half-saturated ammonium

[43] Z. Unters. Nahr. Genussm., 1918, 36, 262 ; J., 1919, 382A.
[44] Chem.-Zeit., 1919, 43, 555 ; J., 1919, 874A.
[45] Amer. J. Pharm., 1919, 91, 594 ; J., 1919, 874A.
[46] J. Ind. Eng. Chem., 1919, 11, 555 ; J., 1919, 509A.
[47] J. Ind. Eng. Chem., 1919. 11, 443 ; J., 1919, 434A.
[48] J. Amer. Chem. Soc., 1919, 41, 107 ; J. Inst. Brew., 1919, 25, 179.

sulphate solution whilst the iodine compounds with the dextrins are soluble, and it is on these facts that the author bases his method. The details of procedure are given rather fully in an abstract in the Journal of the Institute of Brewing and the reader is referred to that journal for further information.

Phosphoric Acid.

The method of titration with alkali using two indicators (cp. Smith ; [49] also Fiehe and Stigmuller [50]) is adapted by W. Wollmer [51] to the estimation of phosphoric acid in the ash of barley, malt, wort, or beer. The method has the advantage of speed over the usual gravimetric molybdate determination, but by its nature it is of doubtful accuracy and moreover the presence of quantities of iron, alumina, manganese, or borate seriously affects the results.

Nuclein Content of Yeast

Jebbink's method for this determination is the hydrolysis of the material with pepsin and hydrochloric acid, the acid content of the solution being 0·2%. The insoluble residue consists of nuclein which is estimated by means of a phosphorus determination. C. A. Lubsen [52] has tested Jebbink's method and finds that it gives accurate results even when solutions containing as much as 0·35% of hydrochloric acid are used, thus disproving Grijns' criticism that long digestion with 0·1% hydrochloric acid partially dissolves some of the nuclein, causing low results.

Malt.

In a note by L. C. Wilson and A. L. Minchin [53] it is suggested that in the estimation of the diastatic power of malt it is unnecessary to extract the malt for three hours, as one hour's extraction with frequent stirring gives the same results. The authors evidently have not consulted previous work on the subject as this was pointed out by J. S. Ford and J. M. Guthrie. [54]

A lengthy paper dealing with the determination of moisture in malt has been published by T. J. Ward, [55] in which the influence of various factors such as the oven, dishes, desiccator, grinding of malt, state of atmosphere, etc. are considered. It seems somewhat strange that the author trusts to adventitious ventilation instead of passing a regulated current of dried air or inert gas through the ovens.

[49] *J.*, 1917, 415.   [50] *J.*, 1912, 943.
[51] *Z. ges. Brauw.*, 1918, **41**, 145; *J.*, 1919, 86A.
[52] *Pharm. Weekblad*, 1918, **55**, 1625; *J.*, 1919, 87A.
[53] *J. Inst. Brew.*, 1919, **25**, 65; *J.*, 1919, 299A.
[54] *J. Inst. Brew.*, 1905, **11**, 206.
[55] *J. Inst. Brew.*, 1919, **25**, 335; *J.*, 1920, 127A

BARLEY AND MALT.

Bode [56] advocates the partial drying of barley which has to be stored for any length of time (an already, well-established procedure in this country), which in his opinion may compensate for any deficiency of sun-drying during the ripening process ; he also states, what is already well known, that this treatment gives better grain for sowing purposes. Studies on the ripening process of barley and other grains have been conducted by A. Reichard [57] by applying the methods of alkaline titration, worked out previously.[58] The finely-ground grain is mashed in presence of sufficient alcohol to destroy its enzymic activity and then titrated under prescribed conditions, the acidity being measured as (*i*) litmus acidity, (*ii*) phenolphthalein acidity, and (*iii*) amino-acid. According to the author the litmus acidity (*i*) represents the more strongly acid substances in the grain, the phenolphthalein acidity (*ii*) the more weakly acid substances, including acid phosphate and some amino-acid, and lastly (*iii*) substances of the amino-acid class alone. By mashing without alcohol and noting the increase of acidity (*iii*) some measure of the enzymic activity of the grain can be obtained.   By estimating these acidities at different stages the author was able to show that the acidity (*ii* + *iii*) diminishes fairly rapidly during ripening, and that a further slight decrease occurs during storage. This represents a conversion of amino-acids into reserve proteins.   This decrease in acidity (*iii*) corresponds in a general way with increased germinative power of the grain.   A close correspondence between germinative power and enzymic activity was noticed.

In some cases, however, the enzymic activity decreases on continued storage even though there is no change in the germinative power.   The author suggests that this decrease is due to the enzymes undergoing a process of condensation, possibly being transformed into zymogens. The action of rain on ripening grain retarded the synthesis of reserve proteins.   A rain-damaged barley was found to be very defective in germinative power and enzymic activity.   The action of rain on the fully-ripened grain retarded the disappearance of amino-acids, though the germinative power was unimpaired.   In giving the results of these observations the author points out that the relations studied appear to be so influenced by various factors, that conclusions cannot be drawn till data have been obtained covering a number of years—normal and abnormal.   It seems unfortunate that the methods used in this exhaustive investigation were not supplemented by the determination of the true hydrion concentrations.   A. R. Ling [59] publishes a fair

[56] *Tageszeit. für Brauerei*, 1918, **16**, 403 ; *J. Inst. Brew.*, 1919, **25**, 213.

[57] *Z. ges. Brauw.*, 1918, **41**, 212 ; *J. Inst. Brew.*, 1919, **25**, 76.

[58] See *Ann. Repts.*, **2**, 421.

[59] *J. Inst. Brew.*, 1919, **25**, 288 ; *J.*, 1920, **128A.**

number of analyses of barleys and the corresponding malts. He states that, as this work is merely preliminary and also a guidance to work in the future, he has not sufficient data to make any generalisations. The results are very interesting inasmuch as they are the first to be published on such a scale and, despite the fact that the life-history of the barleys is unknown, they furnish a valuable contribution to the proximate increase and decrease of the constituents of barleys and the malts obtained therefrom, changes which, however, must always be more or less a function of the conditions of growth.

C. A. Nowak [60] claims to reduce the time of germination of barley by one day and increase the extract of the resulting malt by about 1% by aerating the barley during steeping without the addition of lime water. When " cast " the barley is sprinkled with 0·1-0·4% solution of phosphoric acid. In view of A. J. Brown's work it seems more probable that the variation is due to the aeration and not to the phosphoric acid. (See also F. Lehmann, *Ann. Repts.*, 1917, **2**, 426.)

HOPS.

R. Heinzelmann [61] gives a lengthy *résumé* of the recent advances made in the chemistry, analysis, treatment, and storage of hops. The question of storing hops has been studied by L. Briant [62] where pockets of the same hops were kept at temperatures ranging from 55° F. to 83° F. over a period of twelve months. His results were as follows : The deterioration in 3 months at 83° was equal to that in 12 months at 55° ; in 5½ months at 75° slightly greater than that in 12 months at 55°, and in 5½ months at 65° midway between 5½ months at 75° and 12 months at 55°.

Continuing his researches at East Malling Fruit Research Station, E. S. Salmon [63] carried out a long series of experiments on thirteen new varieties of hops. His valuable information is grouped under six headings :—(1) Origin of the new varieties. (2) Actual and estimated yields. (3) Number of bushels required to the cwt. (4) Evaluation of samples by experts. (5) The resin-contents. (6) General summary. The general conclusion arrived at on studying Salmon's work is the great difference, in many ways, of the hops under examination, a fact which makes it obvious that his researches should be studied carefully by hop-growers, merchants, and brewers alike. From experience in regard to the chemical analysis of hops for antiseptic value the present writers are of opinion that more value would have been obtained had the resins been estimated separately and not merely classed as soft and

[60] *Pure Products*, 1918, **14**, 219 ; *Bull. Agric. Intell.*, 1918, **9**, 1241 ; *J.*, 1919 86A.
[61] *Woch. Brau.*, 1918, **35**, 207 ; *J. Inst. Brew.*, 1919, **25**, 78.
[62] *Brewing Trade Review*, Jan., 1919, **8**.
[63] *J. Inst. Brew.*, 1919, **25**, 189.

hard. From a little-noticed paper by R. Siller [64] and the researches of A. J. Brown and his collaborators [65] a reliable method for the antiseptic evaluation of hops may be devised.

G. A. Russel [66] carried out field tests during three successive years on an upland and a sandy loam soil, the effect of irrigation being also studied. The total amount of soft resins showed a large increase on the irrigated fertilised soil, but this was due to the increased growth of the hops, the percentage of resins in the hops being decreased. No marked superiority of a particular fertiliser or combination of fertilisers in regard to the yield of available soft resins per acre was found.

In continuance of their work on the use of ammonium polysulphide as a protection against powdery mildews, J. V. Eyre, E. S. Salmon, and L. K. Wormald [67] now find that the resistance of the hop mildew depends on the stage of its development. By intermittent washing with the strength of solutions of ammonium polysulphide prescribed the mildew can be successfully destroyed.

BREWING AND BREWING MATERIALS.

Waters.

P. Petit, [68] dealing with the influence of brewing water on the production of hazes (glutin) in beer, shows that carbonates in water, by neutralising the natural acidity of the wort, render less complete the precipitation of proteins in the copper during boiling. The acidity, which increases in the subsequent process of fermentation, precipitates these proteins. Reference is made to a previous paper [69] by the author on the treatment of beers with proteoclastic enzymes showing that good results have been obtained by a number of French brewers by this means.

Continuing their work [70] on the interaction of the salts of brewing water with the salts of malt. W. Windisch and D. Goldacker [71] publish a long paper describing various experiments with salts and discussing the probable course of the reactions and their influence on brewing processes. Many of their conclusions are already well known and some of their opinions are quite at variance with practical experience under the conditions which obtain in this country.

[64] Z. Unters. Nahr. Genussm., 1909, 18, 241.

[65] J. Inst. Brew., 1910, 16, 641; 1913, 19, 261.

[66] J. Ind. Eng. Chem., 1919, 11, 218; J., 1919, 265A.

[67] J. Bd. Agric., 1919, 25, 1494; J. Inst. Brew., 1919, 25, 213; J., 1919, 335A.

[68] Brasserie et Malterie, 1918, 8, 297.

[69] Ibid., 1916, 16, 161; J. Inst. Brew., 1916, 22, 468.

[70] Ann. Repts., 1917, 2, 427.

[71] Woch. Brau., 1919, 36, 1; J. Inst. Brew., 1919, 25, 274; see J., 1919, 594A.

Malt substitutes.

A. Cluss and V. Koudelka [72] have investigated the use of beetroot as an adjunct to malt in brewing. . From observations in the laboratory and in practice they conclude that this substitute gives quite good results if care be taken to add the beetroot or the juice to the mash *after* saccharification is complete. This precaution is essential owing to the influence of beetroot on the saccharifying enzymes of the malt. F. Koritschoner [73] gives a general analysis of the sugar beetroot which he finds consists of 94-96% of juice and 4–6% of fibre ; the juice contains 82–85% of water, 1·5–2·0% of organic non-sugar, and 0·5–1·0% of mineral matter. The non-sugar portion contains the following :— Oxalic, malic, citric, malonic, succinic acids, pectin, colouring and aromatic substances, glutaminic acid, glycocoll, asparagine, betaine, proteins, and inorganic salts. The average composition of dried beetroot slices he gives as follows :—Water, 7·86 ; crude protein, 4·52 ; fat, 0·56 ; fibre, 4·4 : non-nitrogenous extract, 78·58 ; sugar, 64·41%. The same author [71] finds that malt diastase is neither weakened nor destroyed by beetroot which has not gone acid to any extent. By extracting the beetroot with water high in carbonates no prejudicial effects are noticeable.

P. Lindner [75] suggests using the bran from flour-mills for brewing, and the utilisation of the spent grain for cattle-fodder. The wort obtained by saccharifying the bran mash with malt extract, having a high nitrogen content, could be used for making bakers' yeast, etc.

Carbonated and bottled beers.

The public demand for carbonated beer is on the increase and much work has been done on the subject during the period under review.

In a short paper on the effect of air in the gas used for carbonating beer, A. R. Ling [76] points out the influence of air on the reproduction of yeast. He states that carbon dioxide used for carbonating purposes should not contain more than one part of air per thousand. Following up the observation of Lindner,[77] P. Petit [78] carried out experiments in which bottles were filled under carbon dioxide pressure and cooled to 1° C. The bottles were opened momentarily, sterilised, and air

[72] *Allg. Zeits. f. Bierbrau. u. Malzfabr.*, 1918, **46**, 329 ; *J. Inst. Brew.*, 1919, **25**, 273.

[73] *Brau- u. Malzind.*, 1918, **19**, 225 ; *J. Inst. Brew.*, 1919, **25**, 274.

[74] *loc. cit.*

[75] *Tageszeit. f. Brauerei*, 1918, **16**, 715 ; *Z. ges. Brauw.*, 1919, **42**, 49 ; *Inst. Brew.*, 1919, **25**, 274.

[76] *J. Inst. Brew.*, 1919, **25**, 173 ; *J.*, 1919, 299A.

[77] *Woch. Brau.*, 1918, **35**, 225 ; also *Ann. Repts.*, 1918.

[78] *Brasserie et Malterie*, 1919, **8**, 345 ; *J. Inst. Brew.*, 1919, **25**, 184.

blown in before the bottles were stoppered again. As a result of this
treatment the stability of the beer was diminished by several days.   F.
Schönfeld [79] found that under certain conditions carbonating causes the
separation of certain colloidal particles ; also that the addition of a
large volume of water may upset the equilibrium of various colloids
and render them subject to precipitation during carbonation. He
suggests diluting with water saturated with carbon dioxide. Reference
is made to iron sickness caused by having wet iron bottles for containing
the carbon dioxide and the author advises obtaining dry bottles from
the manufacturers.

Low-gravity beers.

Prior to the partial removal of the restrictions referred to in the
introduction, much work had been done on the subject of low-gravity
beers. The many difficulties encountered by the brewer were success-
fully surmounted. In a number of cases the results were as one would
have expected in view of our knowledge of yeast reproduction and
nutrition, and it was probably due to the application of this knowledge
that beers of such low gravities were so successfully produced. H. B.
Wooldridge [80] states that the amount of yeast used at pitching is of
fundamental importance in regard to the yeast outcrop. He found,
as was anticipated, that much less yeast was necessary with low-
gravity beers than with the beers of pre-war days.

H. L. Hind and J. L. Baker [81] tabulate the analyses (original and
apparent gravities) of ten different beers collected at Belgian and
German breweries between December 1918 and February 1919. The
German beers were brewed before the districts were occupied by the
British and the Bavière was brewed at Brussels during the German
occupation. The original gravities varied from 1001·02 to 1013·86,
showing the state of affairs prevalent at the time in question.

Notwithstanding the dilution of the worts, F. Schönfeld and H. Krum-
haar [82] state that yeast may be used through a considerable number of
fermentations without showing any diminution in nitrogen- or mineral-
content, and also remain free from infection. Some crops were found
to have a high nitrogen-content and the authors attribute this to the
fact that, owing to less evolution of carbon dioxide. the yeast remained
comparatively quiescent and did not multiply.   F. Schönfeld and C.
Goslich [83] found that yeasts obtained from worts of a gravity of 1023
possessed a higher " working power " than those produced from higher

[79] *Tageszeit. für Brauerei*, 1918, **16**, 673 ; *J.*, 1919, 300A.
[80] *J. Inst. Brew.*, 1919, **25**, 171 ; *J.*, 1919, 299A.
[81] *Ibid.*, 1919, **25**, 205 ; *J.*, 1919, 508A.
[82] *Woch. Brau.*, 1918, **35**, 213 ; *J.*, 1919, 300A.
[83] *Ibid.*, 1918, **35**, 201 ; *J.*, 1919, 154A.

gravities and the authors account for this observation from the fact that low-gravity fermentations are usually arrested at an earlier stage and are thus in a very vigorous condition. They also state that the nitrogen-content of the yeast so obtained is high, and this is generally indicative of a high "working-power." T. Bokorny [84] studied the multiplication of yeast using different strengths of sugar solutions, in place of worts. He found that a 6% sugar solution was most favourable to yeast reproduction, higher results being obtained with this concentration than with 3, 5·4, 7, and 8% solutions. The present writers, from their experience, do not consider that such results have any direct bearing on brewing conditions ; the multiplication depends also on the nitrogen- and mineral-content of the media.

W. Windisch [85] has investigated the maladies of thin beers and finds that nitrous acid is produced by the action of yeast and bacteria on the nitrates of brewing water. This acid by interacting with such substances as amides and amino-acids produces various organic acids which give rise to unpleasant odours and also to turbidity by increase of acidity. Tyrosine when present would yield p-cresol by putrefaction, and this would result in the so-called "carbolic smell." The intermediate products of these actions will give rise to various coloured substances which would be noticed in the beer. By the action of nitrous acid on tannin a dark-coloured substance is produced, causing cloudiness. The production of acidity during boiling is therefore of importance as it affects the precipitation of tannin ; this would also apply to hop-resins especially if waters are high in carbonates, when the resins form salts, and these resins are liberated by the subsequent production of acidity. The same author [86] points out some other sources of trouble in the manufacture of light beers. He recommends diluting strong beers instead of brewing at the gravity required finally. With regard to the sterilisation of the water used for diluting he states that it is better to add lime in the cold, thus precipitating the carbonates and iron and carrying down the bacteria. He contends that when the water is boiled, sarcinæ and other acid-forming bacteria usually find their way into it during cooling. F. Schönfeld [87] states that where water is used for diluting a fully-conditioned beer the presence of carbonates in the water is of no practical importance, but decarbonation might be advisable when the beers have to be diluted before the actual conditioning takes place, as a high carbonate-content of the dilution water might weaken the yeast during secondary fermentation.

[84] *Allgem. Brauer- u. Hopfenzeit.*, 1917, **57**, 1327 ; through *Z. ges. Brauw.*, 1918, **41**, 210 ; *J.*, 1919, 299A.

[85] *Woch. Brau.*, 1918, **35**, 310 ; *J.*, 1919, 509A.

[86] *Ibid.*, 1919, **36**, 175 ; *J. Inst. Brew.*, 1919, **25**, 321.

[87] *Tageszeit. für Brauerei*, 1918, **16**, 243 ; *Z. ges. Brauw.*, 1918, **41**, 198 ; *J.*, 1919, 155A.

F. Schönfeld and C. Goslich [88] give data regarding the solubility of carbon dioxide in beer. It diminishes with a rise in temperature, fall of pressure, and with a decrease in the content of sugars, dextrins, alcohol, and other constituents which contribute to the viscosity of beer. These data seem only what is to be expected from known physical laws. With regard to the influence of sugar, etc., on the solubility of carbon dioxide reference may be made to the work of A. Findlay and B. Shen.[89] H: Zikes [90] enumerates the degenerative effects of the cultivation of yeast in worts of very low gravities, e.g. 1012–1020, at which gravity the fermentative and reproductive functions are impaired (cp. Schönfeld and Goslich, J., 1918, 779A).

H. L. Hind,[91] in a short paper, gives some idea of the difficulties faced and surmounted by Belgian brewers during the German occupation. The notes tabulated were supplied by the chemist at the Wielemans Ceuppens Brewery at Brussels and show the kind and percentage of malt substitute used in the brewery between 1915 and 1918. The remarks on the various substitutes and how they worked in practice and the type of beer produced are very interesting.

Caramel.

In a short paper on " Nitrogen in Caramel ; its Relation to Ropiness," L. C. Wilson [92] deprecates the use of caramel made by the ammonia process. He gives an instance in which ropy stouts had been general for some time, the caramel was changed and one used in its place in the manufacture of which no ammonia had been used, and immediate beneficial results followed. Dealing with the manufacture of caramel the author concludes by stating, " It is, however, highly desirable from the brewers' point of view, that manufacturers should be limited to the amount of liquid ammonia used, and the interests of the brewing trade safeguarded in regard to the use of this objectionable ingredient which, in my opinion, under certain conditions is likely to lead to the development of ropiness and unsoundness." This does not meet with the views of L. Briant and H. Harman [93] who adhere to the opinion formed in 1912.[94]

YEAST.

In a very able review on " Yeast Growth and Alcoholic Fermentation by Living Yeast," A. Slator [95] deals with the various phases of yeast growth. He divides these into five different classes, namely : (A)

[88] Woch. Brau., 1918, 35, 167 ; J., 1919, 87A.
[89] J. Chem. Soc., 1911, 99, 1313 ; 1912, 100, 1459.
[90] Allgem. Z. Bierbrau. u. Malzfabr., 1918, 46, 21 ; J., 1919, 87A.
[91] J. Inst. Brew., 1919, 25, 57.   [92] J. Inst. Brew., 1919, 25, 174.
[93] Ibid., 1919, 25, 260.   [94] Ibid., 1912, 18, 673.
[95] J., 1919, 391B.

Lag-phase in growth : (B) logarithmic phase ; (c) retarded growth ; (D) yeast crop ; (E) death of cells It is outside the scope of this report to enter into details and the reader is referred to the original.

H. Zikes [96] carried out some experiments on the biology of yeast with pure cultures of four species of bottom-fermentation yeasts of the Frohberg type. He used malt wort and malt wort with the addition of 20% sucrose solution as culture media, and found that the sugar wort mixture promoted the vital functions of the yeast to a greater extent than the malt wort alone. He accounted for his results by certain assumptions as to the different velocities of osmotic diffusion of the mono- and disaccharides.

M. L. Lindet [97] has studied the influence which the vegetative function of yeast exerts on the yield of alcohol. His work covers a variety of conditions of fermentation—the carbohydrate and nitrogenous content of the medium, type of yeast, temperature, duration of fermentation, etc., and is in accordance with the work of T. E. Thorpe and H. T. Brown [98] in their investigations when compiling the new tables for the determination of the original gravity of beers. Lindet's work is being continued.

According to the present state of our knowledge Wildier's discovery [99] in 1901 was not so premature as was thought at first when it is seen how workers of the present day compare the vitamines with his so-called " bios." F. M. Bachmann [100] makes reference to the above in her work. She found that yeasts differ greatly in their capacity for developing and fermenting in an inorganic medium containing sugar. Some grow when introduced only in minute amounts. On the other hand, she found that a yeast, obtained from a sample of fermenting canned pears, was incapable of growth or fermentation even when added in large amounts to a sugar-mineral medium. The addition of some nitrogenous substance was found essential for growth, the most effective substances being milk, yeast broth, and extracts of various vegetables. These materials have been found to be rich in the vitamine fraction known as " water-soluble B " The amount of nitrogenous material required is so small and its effect upon the growth and activity of the yeast so striking as to suggest a similarity between its action and that of the vitamines required for normal animal development. She suggests that yeasts such as the one referred to above might be used to detect, or even determine, the amount of certain vitamines in different materials. R. J. Williams,[101] in his work on the vitamine requirements of yeasts, also presents evidence that the " water-

[96] *Centr. Bakt., II Abt.*, 1916, **46**, 385 ; *J.*, 1919, 839A.
[97] *Annales de la Brasserie et de la Distillerie*, 1919, 85.
[98] *J. Inst. Brew.*, 1914, **20**, 569.   [99] *La Cellule*, 1901, **18**, 313.
[100] *J. Biol. Chem.*, 1919, **39**, 235 ; *J. Inst. Brew.*, 1919, **25**, 374.
[101] *J. Biol. Chem.*, 1919, **38**, 465 ; *J.*, 1919, 692A.

soluble B " fraction, relatively so abundant in yeast, is necessary for the nutrition of yeast cells themselves. E. Abderhalden and H. Schaumann [102] show that various fractions, having diverse degrees of activating power on the fermentation by living yeast and yeast juice, can be prepared by treating an acid extract of yeast with alcohol. One particularly powerful fraction, termed "cutonin," is obtained by precipitating the alcoholic extract with acetone ; this fraction is completely free from phosphorus. The authors suggest that vitamines may resemble these extracted substances in exerting an activating influence on certain enzymic processes in the body.

G. Ellrodt [103] compares the amount of nitrogen assimilable by yeast in beet molasses and grain or malt-combs and states that it is easy to calculate how much nitrogenous matter (e.g. ammonium salts, which are entirely assimilable) must be added to molasses worts to produce a given yeast crop.

BREWERY BY-PRODUCTS.

K. Schweizer [104] details a method whereby brewers' yeast, after being freed from bitterness by treatment with weak alkali, is mixed with various condiments and subjected for a short time to 100° C., at which temperature the so-called vitamines are not destroyed, and the yeast preparation can be used for medicinal purposes as a remedy for beri-beri, rickets, etc. By treating waste yeast with formaldehyde, drying, grinding with or without the addition of tar, tar oils, sulphur, and pigments, and compressing into moulds, a product termed "ernolith " is obtained which can be used as a substitute for bakelite, celluloid, etc. G. Bode [105] points out the importance of utilising brewery by-products to the utmost extent. Malt rootlets can be used not only as yeast food and as cattle-fodder, but also for human consumption, e.g. in the manufacture of soup squares, etc. Spent grains can be used as cattle food. The author advises the co-operation of a number of breweries where, individually, the amount of surplus yeast would not pay for working up. He contends that the demand for yeast in the preparation of foodstuffs will continue for years after the war. W. Volz [106] finds that dogs can digest a larger proportion of the proteins and carbohydrate in brewery yeast than in "mineral " yeast, and that brewery yeast is a preferable adjunct to the fodder of sheep.

[102] Fermentforsch., 1918, 2, 120; from Chem. Zentr., 1918, II., 737; J. Chem. Soc., 1919, i, 108.
[103] Brennereizeit., 1918, 35, 8183; Chem. Zentr., 1919, 90, IV., 46; J., 1919, 786A.
[104] Schweiz Chem.-Zeit., 1919, 1, 33; J., 1919, 433A.
[105] Woch. Brau., 1918, 35, 219; J. Inst. Brew., 1919, 25, 224.
[106] Ibid., 1919, 36, 43; ibid., 1919, 25, 273.

BACTERIOLOGY.

Outstanding in this particular section of the fermentation industry is the contribution by A. C. Chapman [107] on " The Employment of Micro-organisms in the Service of Industrial Chemistry. A Plea for a National Institute of Industrial Micro-biology." The writers are well aware of the importance of such a contribution, but deem it unnecessary to enter into details and only hope that the paper bears the fruit it so richly deserves.

C. Barthel [108] carried out experiments using sterilised soil as a medium for the cultivation of various fermentation organisms, and found that these organisms grew quite as well in soil as in wort provided the moisture content of the soil did not fall below 10%. This treatment had no weakening effect on the capacity for growth.

ACETONE.

The demand for acetone as a solvent in the manufacture of cordite and for other purposes increased enormously during the war, and to meet this, much original research in biological, organic, and inorganic chemistry was carried out practically all over the world.

H. B. Speakman [109] deals with certain features of the work of producing acetone at the British Acetones plant in Toronto, Canada. At the Conference on Recent Developments in the Fermentation Industries, Col. Sir F. Nathan [110] gave a brief historical retrospect on the manufacture of acetone, and A. Gill [111] detailed the fermentation process. The writers in this Report can only refer the reader to the originals for fuller information. Without entering into the controversial side of the question in connection with the production of acetone by fermentation methods, the original work of Fernbach calls for recognition.

J. H. Northrop, L. H. Ashe, and J. K. Senior [112] isolated an organism from old potatoes which is capable of producing acetone and ethyl alcohol from starch or sugar. They termed this new organism *Bacillus acetoethylicus*. The optimum temperature was found to be 43° C., and the best results obtained when the media were adjusted to P_H^+ 8–9. The other non-gaseous products of the fermentation are ethyl alcohol and formic acid. Under the conditions employed by these authors the maximum yield of acetone and alcohol is reached in from seven to nine days. Maize meal was found to be the most favourable raw material for use on a commercial scale. The influence of the addition of nitrogenous material, variations in the air supply and concentration were studied. The addition of nitrogenous material, such as yeast or pep-

[107] *J.*, 1919, 282T.
[108] *Centr. Bakt.*, 1918, **48**, 340.
[109] *J.*, 1919, 155T.
[110] *Ibid.*, 271T.
[111] *Ibid.*
[112] *J. Biol. Chem.*, 1919, **39**, 1; *J.*, 1919, 734A.

tone, increased the yield of acetone when little air was admitted to the culture. Aërobic conditions yielded an increase of acetone, with, however, a decrease of alcohol. Aeration and addition of nitrogenous substances combined did not increase the yield of acetone. The maximum concentration which fermented completely was 8 parts of maize to 100 parts of water. The authors investigated the fermentation of cane molasses and also describe a semi-continuous method for carrying on the fermentation. J. H. Northorp, L. H. Ashe, and R. R. Morgan [113] describe a process which they have patented, and dedicated to the public use.[114] In this process the same organism as above is used.

An organism isolated from slaughterhouse runnings is used by E. Richard [115] for the manufacture of acetone and butyl alcohol from maize. A mash of 8–9% is inoculated with a vigorous culture of the organism, designated *Bacillus butylicus* B.F. (Boinot Firmin), and allowed to ferment for 24–26 hours. The combined yield of acetone and butyl alcohol is 38–40% of the starch or sugars originally present, the ratio being one part of acetone to two parts of butyl alcohol.

<center>GLYCEROL.</center>

Although Pasteur, in 1858, proved the presence of small amounts of glycerol in the products of alcoholic fermentation, glycerol has hitherto been regarded as outside the province of the fermentation industries. The necessities of war and the shortage of fats occasioned by our blockade compelled the Germans to seek for some other means of producing this all-important explosive base. Much has been made of the manner in which they overcame their difficulties, but considering the urgency of the situation and the already recognised observations their achievement is not so remarkable after all. When it was reported in 1917 that the Germans were producing large quantities of glycerol by a fermentation process, investigations were undertaken in four different laboratories in America, and although there was not the same incentive for immediate success the American chemists were not long in finding a partial solution to the problem and have actually carried out experiments on a large scale. Their method so far has not given so great a yield as that obtained by the Germans, but it must be remembered that they do not claim to have reached finality, and in all probability would have effected many improvements had the signing of the armistice been delayed. For further details of the work of J. R. Eoff, W. V. Lindner, and G. F. Beyer,[116] the reader is referred to the Report of the Chemistry Division of the U.S. Bureau of Internal Revenue, May 8, 1918,[117] and also to a very able and comprehensive

[113] *J. Ind. Eng. Chem.*, 1919, 11, 723; *J.*, 1919, 786A.
[114] U.S. Pat. 1293172; *J.*, 1919, 334A.
[115] Eng. Pat. 130666; *J.*, 1919, 787A.
[116] *J. Ind. Eng. Chem.*, 1919, 11, 842; *J.*, 1919, 786A.   [117] *J.*, 1919, 383A.

review by A. R. Ling,[118] who records and summarises much of that report.

Regarding the German process an account is given by the originators, W. Connstein and K. Lüdecke.[119] It was found that if the fermentation of sugar by means of yeast was carried out in a slightly alkaline medium, the yield of glycerol, which ordinarily is about 3% of the sugar fermented, is augmented. Later it was observed that large quantities of non-toxic salts in general, such as aluminium sulphate, calcium chloride, sodium acetate, chloride, nitrate, and sulphate, etc., have the same effect. The difficulty of preventing the growth of certain bacteria led to the adoption of sodium sulphite which, besides being antiseptic and yet tolerated by the yeast, is slightly alkaline and substantially increases the production of glycerol. When the amount of sodium sulphite used is 40% of the sugar present, the proportion of glycerol is 23·1% of the sugar fermented. By increasing the sulphite to 100 and 200% of the sugar the yield is raised to 30 and 36·7%. With high proportions of sulphite, however, the fermentation becomes slow and the yeast is permanently injured. Acetaldehyde is also a product of the fermentation; the larger the proportion of sulphite used the more aldehyde is formed and the smaller the production of alcohol and carbon dioxide. The output of glycerol by this method in Germany was 1000 tons per month. The yield was between 20 and 25% of the sugar employed. In addition large quantities of acetaldehyde and alcohol were obtained as by-products.

DISTILLING AND ALCOHOL MANUFACTURE.

A feature of this important section of the fermentation industry is the number of substances used in the manufacture of alcohol and the processes involved in rendering those substances fit for fermentation by yeast.

B. Kazmann [120] utilises roasted or burnt cereals and other amylaceous matter, e.g., the residues from the manufacture of coffee substitutes, which, owing to the presence of substances injurious to yeast, have not been used before. The material is washed with hot water, cooled, and treated with diastatic substances. The whole mash, or liquid portion only, is subsequently heated with sulphuric acid to convert any dextrins into sugar, fermented with yeast, and the alcohol recovered by distillation. R. H. McKee [121] claims to produce alcohol from waste sulphite liquors or the fermentable syrups or liquors obtained from cellulose or ligno-cellulose. The liquors are cooled and partially freed from

[118] J., 1919, 175R.   [119] Ber., 1919, 52, 1385; J., 1919, 691A.
[120] Eng. Pat. 119333; J. Inst. Brew., 1919, 25, 225. See U.S. Pat. 1267081; J., 1918, 558A.
[121] Eng. Pat. 120520; Ibid, 1919, 25, 227. See U.S. Pat. 1273392; J. 1919, 600A.

sulphur dioxide by aeration (down to 0·35 grm. sulphur dioxide per
litre), pitched with yeast, and the fermentation carried on in a moderate
current of air.   The alcohol is then distilled off, being preferably freed
from any sulphur dioxide by treatment with alkali in course of the
distillation process.   The fermentation gases may be scrubbed with
unfermented liquor, in order to prevent loss of alcohol.

Mannocellulose, which is contained in large amounts in vegetable
ivory, on being boiled with dilute mineral acid, is converted into man-
nose, and this sugar is fermented by selected wild yeasts occurring in
Perugia. G. Mezzadroli gives details [122] of a process where 10-15
litres of alcohol is produced from 100 kilos. of raw material, usually
the waste from the works where buttons are manufactured from the
vegetable ivory. Mould fungi of the type of *Mucor Rouxii* will also
effect the decomposition of the mannocellulose, but a higher temperature
and pressure and a longer time are required than when mineral acids
are used.

An account is given by Laskowsky [123] of the operation of a plant
for the production of alcohol from sawdust by Classen's process which
was worked in this country twelve years ago.   The author maintains
that, with the recent improvements in the process, it should be possible
to get 10–12 litres of alcohol from 100 kilos. of raw material (about
double the old yield).   The residue from the lixiviating plant could
be used for mixing with molasses and with evaporated spent-wash for
fodder purposes.

E. Kayser [124] makes use of marine algæ for the production of alcohol.
By treating *Laminaria flexicaulis* and *L. saccharina*, cut into small
pieces, with 7% sulphuric acid, and bringing the liquid to an acidity
of 0·1% before fermentation, yields of 12 litres of alcohol per 100 kilos.
of dry algæ were obtained.

The yield of alcohol obtainable in tropical distilleries in the fermenta-
tion of cane molasses under different conditions of working has been
studied by J. Magne. [125]

SPIRITS.

On the subject of the production of German whisky E. Duntze [126]
states that potato-spirit of 40–50% alcoholic strength, filtered or not
filtered, was stored under various conditions for three or four years in
casks made of fresh " Slavonic oak " and also in carbonised casks.   The
results showed that potable spirits equal in quality to well-known

[122] *Boll. Chim. Farm.*, 1918, **57**, 361 ; *J.*, 1919, **38**, 59A.

[123] *Chem.-Zeit.*, 1919, **43**, 51 ; *J.*, 1919, 193A.

[124] *Anr. Chim. Analyt.*, 1919, **1**, 79 ; *J.*, 1919, 266A.

[125] *Louisiana Planter*, 1917, **59**, 13 ; *Intern. Sugar J.*, 1919, **21**, 466 ; *J.*,
1919, 786A.

[126] *Deutsche Essigind.*, 1919, **23**, 67 ; *Chem. Zentr.*, 1919, **90**, II., 679 ; *J.*, 1919,
594A.

foreign (non-German) brands can be produced in this way, filtration and storage in carbonised casks conferring mildness of aroma and flavour. The spirit used in these experiments was practically free from fusel oil.

WINES.

A criticism of the French official method for the analysis of wine and also some suggestions for improvement is given by P. Malvezin.[127] For the estimation of the total solids he proposes the following method. Fifty c.c. of wine is evaporated in a flask connected to a water pump, and heated in a water bath at 75° C. When the residue attains a pasty consistency a current of steam is passed through the flask for one hour, after which the solids are dried at 100° C. under reduced pressure for about ten minutes. By this treatment the author claims that all the glycerol is removed, which is not the case in many methods, including the French official. Regarding the methods for the estimation of the other constituents of wine, those for alcohol, potassium sulphate, and reducing sugars (gravimetric) are considered reliable, but the separation of fixed and volatile acids leaves much to be desired. For the volatile acidity the author favours the application of Duclaux's method. For a rapid determination of tartaric acid in wine L. Mathieu[128] describes a method originally proposed by Pasteur in 1873. The same author[129] discussing the proposal to add magnesium sulphate to agglomerate the precipitate in the volumetric estimation of reducing sugar (cp. Lenk[130]), states that in operating with wines he adds one gramme of barium sulphate for a similar purpose, the reaction liquid being boiled in a wide tube and the end point judged visually from the colour of the solution.

M. Canonica[131] proposes a new method for the estimation of glycerol in wines. He submitted his method to tests on wines with high and low sugar-content before and after the addition of a known quantity of glycerol; also on wines with no sugar before and after the addition of 1% sugar. Concordant results were obtained.

G. Halphen[132] states that the Halphen ratio (the minimum ratio of alcohol to acid) for Italian wines is practically the same as for French, Algerian, and Tunisian wines. He replies to the criticism of Scurti and Rolando[133] by suggesting that their interpretation of this ratio is not the same as that in France.

One of the wine diseases, vins tournés, is caused by certain bacteria,

[127] Ann. Falsif., 1919, 12, 147; J., 1919, 692A.
[128] Ibid., 1919, 11, 80; J., 1919, 475A.
[129] Bull. Assoc. Chim. Sucr., 1919, 37, 49; J., 1919, 839A.
[130] J., 1917, 934.
[131] Anal. Soc. Quim. Argentina, 1918, 6, 94; J., 1919, 114A.
[132] Ann. Chim. Analyt., 1919, ii, 1, 185; J., 1919, 594A.
[133] J., 1917, 1284.

the symptoms generally being turbidity, formation of sediment, change in colour, and an increase in volatile acidity. An explanation of these changes is given by L. Roos [134] in a suggestive discourse. He states that the increased volatile acidity is due to the decomposition of tartaric acid which is apparently converted into tartronic, lactic, and propionic acids and carbon dioxide. Thus wine badly attacked may be quite free from tartaric acid, and the amount of the latter cannot therefore be used as a basis for the detection of added water in the wine. Generally the altered wine has a particularly high mineral content, since further amounts of potassium bitartrate dissolve from the cask walls as the decomposition of the already dissolved tartrate proceeds. An indication of water adulteration is obtained when exceptionally low results are found for the total ash, alkalinity, and total potassium.

W. Schulte [135] describes in detail some analytical methods for the recognition of cider, currant wine, etc. in genuine wines. He points out that tartaric acid is present in considerable quantities in wine, while only traces are to be found in cider and the " berry " wines. In connection with this observation Pratolongo [136] states that natural wines form a saturated solution of potassium bitartrate and calcium tartrate, and using these facts as a basis he suggests a method for the detection of added water to wines. Schultze remarks that citric acid is not a constituent of genuine wines, but is present in cider, gooseberry, currant wines, etc. Regarding the statement that citric acid is found in cider W. J. Baragiola, O. Schuppli, F. Braun, and J. R. Kleber, [137] who record the analyses of 28 samples of cider, find that citric acid was absent. The latter authors also refer to an unidentified acid which Schulte found in wines and suggest that it is lactic acid.

For the estimation of the higher alcohols in wines J. Trambics [138] uses a modification of the Allen-Marquardt method. He uses 400 c.c. of the sample, makes six extractions with carbon tetrachloride, and for the final titration uses $N/10$ sodium hydroxide free from carbonates. These are his essential differences although minor details of the process are likewise modified. Applying this method to pure ethyl alcohol only 0·04% amyl alcohol was indicated as against 0·12% by the original Allen-Marquardt method. Included in the paper are the results for higher alcohols of sixteen samples of Hungarian red and white wines.

A paper of theoretical and practical importance is that by A. Borntraeger, [139] who has studied the reaction between potassium bitartrate

[134] *Ann. Falsif.*, 1918, **11**, 300; *J.*, 1919, 25A.

[135] *Chem.-Zeit.*, 1918, **42**, 537, 557; *J.*, 1919, 114A.

[136] *Staz. Sper. Agrar. Ital.*, 1918, **51**, 56.

[137] *Z. Unters. Nahr. Genussm.*, 1918, **36**, 225; *J.*, 1919, 382A.

[138] *Ibid.*, 1917, **34**, 467; *J.*, 1919, 786A.

[139] *Annali Chim. Appl.*, 1919, **11**, 6; *J.*, 1919, 839A.

and calcium sulphate in the fermentation of plastered grape must, and as a result of many experiments, concludes that potassium bisulphate is not formed in the process. In a further contribution the same author [140] describes the reaction between potassium sulphate and tartaric acid under varying conditions. In contradiction to the commonly accepted belief that plastered wines contain potassium bisulphate or free sulphuric acid, originated by Bussy and Buignet,[141] the author shows that the proportion of potassium bitartrate and calcium sulphate taking part in the reaction corresponds with the formation of normal potassium sulphate as found by Chancel.[112] He further proceeds to give the reactions taking place during the evaporation of wine and in the subsequent drying of the residues. Finally, commenting on his experiments regarding the detection of free sulphuric acid in wines, he summarises the behaviour of potassium bisulphate and tartaric acid with alcohol and ether. Space considerations preclude further reference, but sufficient has been written to show the important character of the work.

M. Ripper and F. Wohack [143] have continued their work [144] on the micro-analysis of wines. Known methods of determining the acids in wines have been adapted to operation with very small quantities of the sample, in most cases 2 c.c.

VINEGAR.

During the war the importance of the vinegar industry increased enormously, the increase in fact being *pari passu* with the demand for acetone. As a result the then existing plant was totally inadequate to meet the huge requirements of the acetone manufacturer so that numerous additions to existing works were made and new plants erected. More particularly was this the case in America where, owing to the favourable situation of that country with regard to supplies of raw material for the acetone fermentation, the bulk of this important munition was manufactured. With the reduction of the demands for explosives comes the question of utilising this continued large output of vinegar. A suggestion from an American writer, P. Hassock,[145] is that acetic acid could be used in place of tartaric and citric acids as an acid base for summer drinks. The question does not really concern this country, for according to a review on malt restrictions and the vinegar industry by C. A. Mitchell,[146] the manufacturers have great

[140] *Annali Chim. Appl.*, 1919, 12, 1 ; *J.*, 1919, 839A.
[141] *Comptes rend.*, 1865, 60, 200.
[142] *Comptes rend.*, 1865, 60, 408.
[143] *Z. landw. Versuchs-Wesen Oesterr.*, 22, 15 ; *Chem. Zentr.*, 1919, 90, II. 926 ; *J.*, 1919, 874A.   [144] *J.*, 1917, 350.
[145] *Western Brewer and Jour. of Barley, Malt and Hop Trade*, 1919, 34.
[146] *J.*, 1919, 99B.

difficulty in meeting the present demands and consequently they are unable to preserve stocks for the two or three months' storage which is essential for a stable and otherwise suitable vinegar.

The only papers of importance dealing with the technique of the industry are those of P. Hassock, already mentioned, and of A. Janke and E. Bauer.[147] The latter discusses the effects of varying the conditions of acetification in vinegar acetifiers. P. Hassock enters into detail regarding the advantages of the large generators over the smaller variety and gives much data in support thereof. He also deals with certain technicalities in the various operations, largely based on personal experience.

[147] *Centr. Bakt., II. Abt.*, 1916, **46**, 545; *J.*, 1919, 840A

FOODS.[*]

By H. W. Bywaters B.Sc., Ph.D., F.I.C.,

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The chief feature noticeable in the work relating to foods published during the past year is the large amount of attention which has been given to the subject of vitamines. In the purely scientific journals dealing with chemical physiology, scarcely a number has been published without containing some communication relating to the investigation of these substances, whilst in the popular press frequent allusions have been made to them.

In his recent Cantor lectures [1] on " Problems of food and their connection with our economic policy," H. E. Armstrong called special attention to these substances and laid great emphasis on the need for taking into account quality as distinct from quantity in all matters relating to food. He urged the importance of growing in this country vegetables and other foods containing necessary, though unstable, accessory substances in preference to foodstuffs such as wheat, which could be grown elsewhere and stored here in quantity to meet possible emergencies. At the British Association meeting at Bournemouth, W. D. Halliburton gave a most interesting account of the researches being carried out with the object of introducing vitamines into margarine. Several investigators have endeavoured to probe the mystery of the nature of these substances, but without much success. Their existence can no longer be doubted, but all attempts to lift the veil and identify them have been uniformly unsuccessful. Whilst most chemists regard them as chemical substances of definite although unknown composition, others are inclined to consider them as being like enzymes. All the recent work tends to show that they are of an unstable character.

The systematic investigation of the components of the various common foodstuffs, to which reference was made in the previous report, is being continued, and results of considerable interest are being obtained.

Several reports have now been published of researches concerning various food materials which were carried out during the war, but of

[1] *J. Roy. Soc. Arts,* 1919, **67**, 653, 667, 681 ; *J.,* 1919, 199R.

F F

which the results, for political or other reasons, have hitherto been withheld from publication. Their contents will be noted under the respective headings. which are similar to those in last year's Report.

BREAD, FLOUR, ETC.

The true, physiological value of the proteins in wheat and other foodstuffs is being thoroughly investigated by Osborne, Mendel, and other American workers. They find [2] that for the maintenance of health in the adult the proteins of the entire wheat kernel are intermediate in value between caseinogen and gliadin. The proteins of the wheat embryo are more efficient for maintenance than those of the endosperm, and are much more effective in promoting the growth of the young animal. The proteins of the bran are also of good quality, satisfactory both for maintenance and for growth. The addition of bran to wheat flour or other foods is, however, not advisable,[3] because besides being itself relatively indigestible, it may reduce the digestibility of the wheaten flour or other food, probably owing to the effect of increased peristalsis on absorption.

The proteins of the pea [4] are of low quality. They can be, however, effectually supplemented by zein, but not by gelatin, which indicates that the inadequacy of the pea proteins to maintain health is not due to a deficiency of tryptophan, lysine, or cystine, but to one of the other amino-acids. Peas are fairly rich in fat-soluble A vitamine, but contain less water-soluble B than wheat ; certain essential inorganic constituents are also only poorly represented in peas.

The chief deficiency in the potato [5] is the relative shortage of calcium, sodium, and chlorine ; there is also a lack of fat-soluble A. The quality of the proteins is of the same standard as the cereal proteins.

The chief protein in the coconut [6] is a globulin containing all the amino-acids essential for growth. Coconut press cake has therefore a high nutritive value which is increased by reason of the relatively large amount of vitamines which it contains. The press cake from ground-nuts [7] can also be made to yield a highly nitrogenous flour containing associated antiscorbutic vitamine. Yeast,[8] besides possess-

[2] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1919, **37**, 557 ; *J.*, 1919, 383A.

[3] A. D. Holmes, *U.S. Dept. Agric.*, 1919, *Bull.* 751, 1 ; *Physiol. Abst.*, 1919, **4**, 331.

[4] E. V. McCollum, N. Simmonds, and H. T. Parsons, *J. Biol. Chem.*, 1919, **37**, 287 ; *Physiol. Abst.*, 1919, **4**, 131.

[5] E. V. McCollum, N. Simmonds, and H. T. Parsons, *J. Biol. Chem.*, 1918, **36**, 197 ; *Physiol. Abst.*, 1918, **3**, 522.

[6] C. O. Johns, A. J. Finks, and M. S. Paul, *J. Biol. Chem.*, 1919, **37**, 497 ; *J.*, 1919, 384A.

[7] K. L. Mackenzie-Wallis, *Indian J. Med. Res.*, 1918, **6**, 45 ; *Physiol. Abst.*, 1918, **3**, 518.

[8] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1919, **38**, 223 ; *Physiol. Abst.*, 1919, **4**, 274.

ing an extraordinary large amount of antineuritic vitamine. also contains protein of excellent quality, which has been found to be capable of maintaining the growth of rats for 12 months, when constituting the sole source of protein in the diet.

The paucity of so many proteins in the cystine. tyrosine. and phenylalanine amino-acids suggests that keratin (containing all three in considerable quantities) might be a super-excellent supplementary protein in a diet, provided its pronounced indigestibility could be overcome. C. Brahm and N. Zuntz [9] have tried the effect of adding a partially hydrolysed extract of horn consisting largely of keratin to a diet in which glue was the only other nitrogenous constituent. When only 10% of extract was present, the inadequate glue was transformed into quite satisfactory protein capable of maintaining dogs in nitrogenous equilibrium for considerable periods of time.

The importance of studies such as have been here referred to will be readily perceived by all who are interested in problems of nutrition.

On the more practical side, interesting results have been given by an investigation carried out by R. Whymper [10] during the war on the cause of the production of staleness in bread. Apparently staleness is not due to loss of moisture ; indeed, loss of moisture occurs only slowly, especially from the centre of the loaf. During the first 100 hours after baking, the zone of drying out is very narrow, extending about one inch inwards from the crust. Later, however, moisture begins to diffuse from the centre of the loaf, but at so slow a rate that there is always a pronounced difference between the moisture content of the crumb at the centre of the loaf and that of the crumb beneath the crust. It was noted that during the process of becoming stale the soluble extract of the crumb decreases, and it is thought that staleness is due, at least in part, to the gradual polymerisation of the starch, whereby the more or less gelatinous fresh bread substance becomes transformed into a crumbly material. Probably a certain amount of deposition of solid starch also occurs in the crumb of the bread, which is accelerated if solid starch particles are already existing in the crumb.

In order to obtain good results in bread-making, attention must be paid not only to the quality of the flour and yeast employed, but also to the dough produced by the mixture of these substances with water. It has been shown by L. J. Henderson, W. O. Fenn, and E. J. Cohn [11] that a slight variation in the amount of certain salts present in the dough considerably modifies its rising power. The effect of the addition of acids, bases, or salts to the dough appears to be due not to any action exerted on the yeast cells, but to changes produced in the viscosity of

[9] Deut. med. Woch., 1917, 43, 1062 ; J., 1919, 302A.
[10] British Baker, 1919 ; J., 1919, 417B.
[11] J. Gen. Physiol., 1919, 1, 387 ; J., 1919, 334A.

the dough.   The best bread is produced from dough having a minimum
viscosity ;   the effect of the addition of salts is to increase the viscosity,
and when this takes place the resulting bread is unsatisfactory.   The
hydrogen-ion concentration in the dough is also important as it has been
shown [12] that when it is below a certain limit the circumstances are
favourable for the growth of the bacilli which are chiefly responsible
for the production of ropiness in bread.   When the hydrogen-ion
concentration is above the fixed limit, the growth of these organisms .
is completely inhibited.

Some progress has been made in the direction of preparing a suitable
material from lupins for incorporation into bread.   Lupin seeds cannot
be used directly for bread-making [13] on account of the bitter poisonous
substances which they contain.   The poisonous constituents of the
seeds can be removed by thorough washing with water, and the puri-
fied flour contains about 60% of protein, 10% of fat, and 20% of soluble
carbohydrates.   As it contains no starch, it cannot be used directly
for bread-making, but when mixed to the extent of 20% with ordinary
rye or wheaten flour, it produces a bread resembling ordinary bread,
although of higher nutritive value because it contains nearly twice as
much protein and more fat.   Various patents have been taken out for
the preparation of lupin flour, whilst both the seed [14] and the pod [15]
have been recommended for the preparation of coffee substitutes.

MILK.

Although milk is generally regarded as the best food for growing
animals, it is not capable of producing good results when it constitutes
the sole article of diet.   Some interesting experiments are recorded by
A. C. McCandlish [16] on two calves which were fed exclusively on whole
milk.   Good results were obtained until the animals were about three
months old, but from then on both gave evidence of insufficient nourish-
ment, and died at the end of about another three months.   The failure .
of milk as a permanent diet for ruminating animals is shown to be due
not to the fact that its nutritive constituents are present in improper
quantities or are poor in quality, but to the inability of the animals
properly to digest and utilise it, unless provided with some roughage
at the same time.

The digestibility of milk and its products is largely determined by
the size of the curds produced by the gastric juice in the stomach.   This

[12] E. J. Cohn, S. B. Wolbach, L. J. Henderson, and P. H. Cathcart, *J. Gen.
Physiol.*, 1919, 1, 221 ;   *J.*, 1919, 334A.
[13] Pohl, *Z. angew. Chem.*, June 20, 1919 ;   *J.*, 1919, 330R.
[14] H. Thoms and H. Michaelis, Ger. Pat. 307007, 1917 ;   *J.*, 1919, 597A.
[15] H. Thoms and H. Michaelis, Ger. Pat. 305604, 1917 ;   *J.*, 1919, 597A.
[16] *Iowa Agr. Exp. Station, Res. Bull.*, 1918, 48, 1 ;   *Physiol. Abst.*, 1919, 4, 272.

point has been investigated [17] with the help of a human regurgitator who had the unique ability to deliver samples of stomach contents at will. It was found that raw cow's milk produced much harder and larger curds than boiled milk, whilst the presence of extra fat (cream) resulted in the production of very fine soft curds, which, however, were slow to leave the stomach. It is to be regretted that no records are given of experiments with citrated milk, or foods prepared from milk powders.

The occurrence of small but constant amounts of zinc in cow's and in human milk [18] suggests that this element has a rôle to play in nutrition which is at present unrecognised. Traces of zinc compounds have also been detected in egg yolk,[19] oysters,[20] and in the tissues of numerous animals.[21] According to C. Delezenne [21] it is most abundant in tissues rich in cells, such as the thymus ; and it is suggested that it plays a part in cellular enzymic metabolism analogous to that played by manganese in oxidase activity.

Various means have been suggested for detecting the presence or absence of added water in milk. R. Ledent [22] has pointed out that the specific gravity of the milk serum, obtained by adding dilute acetic acid to milk, warming at 70° C., and filtering, varies between very narrow limits, viz. from 1·027 to 1·029 at 15° C. He considers that if the specific gravity is lower than 1·025 the milk must contain added water. Another method of interest [23] is that depending on the determination of the electrical conductivity of milk. Unfortunately, although the specific conductivity of a mixture of milk and water decreases with increased dilution, the decrease is not as great as might be expected owing to the dissociation of the phosphates and citrates in the milk.

Various formulæ have been put forward by L. J. Harris [24] for calculating the amount of added water from the amount of fat and solids-not-fat in the watered milk, but H. D. Richmond [25] maintains that the calculations involved take more time than the operations required by his well-known slide-rule method.

Various synthetic milks have been proposed and patented. In

[17] O. Bergeim, J. M. Evvard, M. E. Rehfuss, and P. M. Hawk, *Amer. J. Physiol.*, 1919, **48**, 411.

[18] [19] V. Birckner, *J. Biol. Chem.*, 1919, **38**, 101 ; *J.*, 1919, 595A.

[20] R. S. Hiltner and H. J. Wichmann, *J. Biol. Chem.*, 1919, **38**, 205 ; *J.*, 1919, 595A.

[21] *Ann. Inst. Pasteur*, Feb. 1919 ; *Physiol. Abst.*, 1919, **4**, 305.

[22] *Ann. Falsif.*, 1919, **12**, 197 ; *J.*, 1919, 787A.

[23] J. H. Coste and E. T. Shelbourn, *Analyst*, 1919, **44**, 158 ; *J.*, 1919, 434A.

[24] *Ann. Repts.*, 1918, 394.

[25] *Analyst*, 1919, **44**, 200 ; *J.*, 1919, 510A ; see also Harris, *Analyst*, 1919, **44**, 314, 317 ; *J.*, 1919, 787A.

one [26] skimmed milk is used as a basis, and a mixture of tallow oil, coconut oil, cacao butter, cod-liver oil, and tallow is added to bring the fat content up to 3·5%. It is said to have been tested on a number of infants with excellent results. Another interesting concoction [27] is prepared by boiling grated coconut with water and mixing it with an aqueous extract of rice or oat meal. The resulting liquid, after treatment with a culture containing the lactic acid bacillus, is offered as a substitute for milk.

FATS.

The shortage of ordinary edible fats during the war has led to a rapid development of the methods for producing palatable edible oils and fats from raw materials which, on account of their peculiar flavour or for other reasons, have so far only been utilised for the production of oils for non-edible purposes, such as soap-making, lubricating, etc. By treatment with hydrogen in the presence of a catalyst, evil-smelling fish oils can readily be converted into solid, odourless, and tasteless fats. The suitability of these hardened fats and oils for edible purposes has been investigated in several directions. It has been found [28] that these unnatural hardened fats are as readily absorbed and assimilated as beef fat. Indeed, except for the fact that the accessory factors (vitamines) are missing, they seem to be as valuable for nutritive purposes as natural fats.

In most of these hardened oils and fats, traces of the catalyst (usually nickel) may be detected, but it has been conclusively shown [28] that such traces of nickel do not have any injurious effect on the body, and, indeed, the trace present is much smaller than that which may be found in foods cooked in nickel vessels. Moreover, large doses of nickel salts may be ingested for long periods without any noticeable ill-effects being produced.

The demand for glycerin during the war resulted in the production of large quantities of fatty acids as by-products in the saponification of fats. A Committee of the Royal Society was appointed to determine whether fatty acids could be utilised in the same way as fats by the animal organism. Various experiments were carried out, and the conclusion drawn [29] was that fatty acids can completely and adequately replace fats in the food. In a series of experiments on rats, the animals were maintained for two months on a diet containing fatty acids, as its sole fatty constituent. It was noted that the animals took their

[26] H. J. Gerstenberger and H. O. Ruh, *Amer. J. Dis. Children*, 1919, **17,** 1 ; *Physiol. Abst.*, 1919, **4,** 272.

[27] J. Piperno, U.S. Pat. 1267449 ; *J.*, 1919, 267A.

[28] W. Fahrion, *Chem. Umschau*, 1919, **26,** 22, 33 ; *J.*, 1919, 510A. Bordas, *Ann. Falsif.*, 1919, **12,** 225 ; *J.*, 1919, 787A.

[29] W. B. Halliburton, D. N. Paton, and others, *J. Physiol.*, 1919, **52,** 328.

food readily, grew healthily, and in some cases bore young. The only
objection which can be raised to the extensive use cf fatty acids in
the diet is that they, like hardened fats and oils, do not contain any
vitamines.

FRUIT.

The various phases in the growth and ripening of fruits have been
subjected to a good deal of study during the past few years. The apple,
considered as a living organism, has been shown [30] to have first a period
of growth, during which the dry matter, presumably starch, is con-
tinually increased. A second or ripening period follows during which
starch is changed into sucrose. This latter substance, in turn, is
gradually changed into invert sugar, whilst at the same time there is
a decrease in the amount of malic acid. Later on, the total amount of
carbohydrate gradually diminishes. These changes are recognised as
due largely to the operation of enzymes. With scarcely any excep-
tion, oxidases can be found in growing fruits. Esterase may also be
present, but diastase and invertase cannot usually be detected.

According to C. Griebel and A. Schäfer [31] certain fruits, particularly
those of the *Pyrus* species, possess a mesocarp consisting solely of tannin
cells. During the mellowing process, the tannin becomes insoluble,
and it is owing to this that the bitter taste of the fruit disappears.

Certain American investigators [32] have sought to throw light on the
changes taking place in the fruit by a study of the changes occurring
in the values of certain physical constants during growth. A close
relationship can be observed between the refractive index, osmotic
pressure, and electrical conductivity and the percentages of sugar and
total solids in the juice. Similar investigations have been carried out
in this country under the direction of the Food Investigation Board.[33]
The changes, both chemical and physical, occurring in the sap of apples
are being observed in fruit stored for various periods both under normal
conditions and also at low temperatures. The sap of the fruit is ob-
tained by cooling portions of the apple in a freezing mixture, and then
expressing the juice with a small hand press. The extract is considered
to be representative of the sap of the fruit. The sap contains only
0·00014 grm. of nitrogen per c.c. of juice, and of this 40%, appears to
be present as ammonium salts, the rest as simple amino-acids. No
trace of protein can be detected in the sap.

Referring to the results already obtained, it has been shown [34] that
non-electrolytes in the sap greatly reduce the electrical conductivity.

[30] W. P. Snyder, *Trans. Ind. Hort. Soc.*, 1916, 408 ; *Physiol. Abst.*, 1919, **4**, 246.
[31] *Z. Unters. Nahr. Genussm.*, 1919, **37**, 97 ; *J.*, 1919, 595A.
[32] R. E. Neidig, C. W. Colver, H. P. Fishburn, and C. L. von Ende, *Idaho Agr. Exp. Station Rep.*, 1917, 22 ; *Physiol. Abst.*, 1919, **4**, 246.
[33] *Report for the year* 1918.   [34] D. Haynes, *Biochem. J.*, 1919, **13**, 111

In deducing the content of electrolytes from the electrical conductivity of such sap, therefore, allowance must be made for the presence of these non-electrolytes.

It is a matter of common observation that when plants or fruits are bruised, browning often occurs. This browning has been shown by M. W. Onslow [35] to be due to the interaction of a peroxidase in the tissues and an aromatic substance giving the reactions characteristic of catechol. When no browning occurs, the substance resembling catechol is absent. Apparently the peroxidase and the catechol substance are in separate cells of the tissues, and it is only when the cell-walls are broken or injured that contact can take place with the production of the brown colour. The catechol substance can be extracted by alcohol, and the peroxidase by water. On mixing the two extracts a brown colour is produced. Plant tissues which on injury do not brown, do not contain the catechol substance.

Attention should also be directed to a method devised by B. T. P. Barker [36] for preparing an extract containing a large proportion of pectins which can be employed for strengthening the jellying power of jams, etc. Vegetable tissues containing pectinous substances, e.g. apple residues from cider manufacture, are disintegrated and, after washing, treated with high pressure steam in order to render the pectins soluble ; these are then extracted with water. The concentrated extract can be stored under sterile conditions or by preserving with sugar without causing it to set.

FISH, MEAT, ETC.

A large amount of attention has been and is being given to the subject of the best methods for preserving animal foods and the changes occurring during their storage or during preservation under various conditions. The Food Investigation Board [33] have taken a pre-eminent part in organising research of this kind. It is well known that one of the best methods of preserving fish is to plunge them into cold brine. Owing to the high specific heat of the brine, the cooling is much more rapid than in the ordinary air-freezing process, and the separation of fluid and solid in the tissues which occurs when the extraction of heat is relatively slow is thereby prevented. The flesh of the fish remains firm when thawed out, and colour and superficial appearance are preserved. The Committee are taking steps to put this process on a commercial basis as they are persuaded that it affords the best method for dealing with gluts of fish at the ports, and at the same time they are investigating the keeping qualities of fish preserved by brine-freezing when stored for long periods of time.

With regard to meat preservation, it has long been known in the

[35] *Biochem. J.*, 1919, 18, 1.   [36] Eng. Pat. 125330, 1918; *J.*, 1919, 436A.

industry that whereas mutton can be frozen without impairing its qualities, beef needs much more careful treatment. Freezing in the ordinary way, that is by cold air, leads to a separation of fluid in the substance of the muscle fibres, with the result that on thawing, unless elaborate precautions are taken, there is loss of water and soluble constituents, and the texture of the meat is impaired. The Committee have therefore decided to inquire into the cause of the peculiar sensitiveness of beef to freezing. Is it, for instance, due to the difficulty of abstracting heat from the tissues of so large an animal as the ox, or is it due to the colloidal properties and the chemical constituents of the muscle fibres themselves ? Is the permeability of the sarcolemma of the muscle fibres of the ox different from that of the sheep ?

Investigation is also being made of the post-mortem changes occurring in meat under various conditions. Under ordinary circumstances, ammonia is one of the most evident substances produced, and K. G. Falk and G. McGuire [37] find that at the ordinary temperature meat becomes unfit for food when the ammonium-nitrogen content reaches 0·3 0·4 mgrm. per gram of meat. At low temperatures, the amount of ammonium nitrogen may be much higher, 1 3 mgrms. per gram of meat. before the meat is unfit. The difference is probably due to the fact that different micro-organisms are at work in the two cases, and in support of this hypothesis it is shown [38] that various bacilli produce different quantities of ammonia when cultivated on meat or meat extract.

A series of interesting experiments has been carried out by G. E. Thompson,[39] who, by means of thermo-couples embedded in the centres of tins of food, has determined the time-temperature curves when the foods are heated to various temperatures by means of hot water or steam. Graphs and formulæ are given by means of which the temperature at the centre of a tin of food can be ascertained practically at any time after the tin has been immersed in the sterilising bath.

TEA, COFFEE, AND COCOA.

An investigation has been carried out by P. Eberhardt [40] concerning the variation in the amount of tannin and alkaloid in the various kinds of tea produced in various countries. Teas from Annam appear to be richest in both substances, whilst Chinese teas are relatively poor.

Various methods have been published during the year for the estimation of cacao butter in cocoa and its related products. Of these reference may be made to a centrifugal process [41] in which the cocoa or

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[37] *J. Biol. Chem*, 1919, **37**, 547 ; *J.*, 1919, 383A.

[38] K. G. Falk, E. J. Baumann, and G. McGuire, *J. Biol. Chem.*, 1919, **37**, 525 ; *J.*, 1919, 383A.   [39] *J. Ind. Eng. Chem.*, 1919, **11**, 657 ; *J.*, 1919, 651A.

[40] *Bull. Agr. Intell.,* 1918, **9**, 1323 ; *Physiol. Abst.*, 1919, **4**, 288.

[41] E. B. Hughes, *Chem. News,* 1919, **119**, 104 ; *J.*, 1919, 735A.

chocolate is extracted first with dilute alcohol and then with a mixture of petroleum spirit and ordinary methylated ether. The ethereal extract is evaporated and the residual fat weighed. Good results are said to be obtained and the method certainly deserves a trial on account of the rapidity with which it can be carried out.

Further attempts have been made to find a satisfactory method for differentiating between the 2% and the 5% of shell in cocoa powders which are the distinguishing features of the grade A and grade B qualities. An empirical method has been proposed by T. von Fellenberg [42] in which the successive treatments with acid and alkali usually employed are replaced by a single boiling with dilute nitric acid. The results for crude fibre which are obtained are similar to those afforded by the ordinary process. F. Mach and P. Lederle [43] have tried to improve the ordinary process by employing a filter consisting of a disc of fine platinum gauze having 16–17 meshes per cm. resting on a porcelain filter plate and covered with a fine layer of asbestos. The fibrous material is apparently more readily retained than by paper.

VITAMINES.

The occurrence of three types of vitamines can now be regarded as fairly well established. They are conveniently referred to as :

(1) Fat-soluble A, or growth-promoting vitamine.

(2) Water-soluble B, or antineuritic vitamine, and

(3) Water-soluble C, or antiscorbutic vitamine.

Fat-Soluble A.

A convenient source of fat-soluble A is butter, although it occurs to a considerable extent in various animal oils, such as whale oil and cod-liver oil. It is also present in many vegetable tissues, and from some of these, such as spinach or clover leaves, preparations rich in fat-soluble vitamine may be prepared [11] by drying in a vacuum or in air, at about 60° C., and then extracting with ether. A green extract is obtained which is mixed with starch and the ether then allowed to evaporate. The resulting dry preparation greatly promotes growth in rats, and quickly causes a renewal of growth in animals previously losing weight on diets deficient in fat-soluble vitamine.

Recent research work [45] tends to, show that this vitamine is more labile than was formerly supposed. When butter or whale oil is exposed to a temperature of 100° C. for as short a time as one hour, the vitamine appears to be completely destroyed. Lower temperatures

[42] *Mitt. Lebensmittelunters. u. Hyg.*, 1918, **9**, 277 ; *J.*, 1919, 596A.

[43] *Chem.-Zeit.*, 1919, **43**, 251 ; *J.*, 1919, 476A.

[44] T. B. Osborne and L. B. Mendel, *Proc. Soc. Exp. Biol. and Med.*, 1919, **16**, 98 ; *Physiol. Abst.*, 1919, **4**, 273.

[45] J. C. Drummond, *Biochem. J.*, 1919, **13**, 81, 95 ; *J* , 1919, 435A.

may also cause destruction, but the process is not so rapid. In the case of whale oil, exposure to 37° for several weeks was found to cause a great diminution in the activity of the accessory factor. As far as could be ascertained, the destruction was not due to changes of an oxidative or hydrolytic nature. Saponification by alkali of oils containing the accessory factor results in the disappearance of the growth-stimulating properties even when the hydrolysis is carried out in the absence of water and oxygen. It has not been found possible to identify fat-soluble A with any known constituents of fats themselves, or with substances frequently associated with fats, such as cholesterol, phosphatides, or pigments, and all attempts to isolate the vitamine in a free condition have been unsuccessful. J. C. Drummond suggests [45] that this vitamine may be of an enzymic nature instead of a chemical substance of comparatively simple constitution.

Although fat-soluble vitamine is generally regarded as an accessory substance essential for the growth of young animals, it is also necessary for the maintenance of health in the adult. Experiments have demonstrated conclusively that the litters borne by rats on a diet deficient in fat-soluble A, although of normal weight at the time of birth, fail to grow at a normal rate, whilst the mortality amongst them is very high. It may be concluded, therefore, that it is particularly important that an adequate supply of the factor should be present in the diet of pregnant and nursing females, because otherwise the milk produced is deficient in fat-soluble A and the infants are likely to be ill-nourished.

The precise rôle which this vitamine has to play in the living organism is still unknown. Rats fed on a diet deficient in this vitamine show no specific pathological lesion, nor does there seem to be any direct relationship between the growth factor and fat-metabolism. The absorption of fat and fatty acids is good in animals which have been deprived of the vitamine for several weeks, and such animals, on post-mortem examination, show apparently normal reserves of body fat. In some cases a distinct lowering in the resistance to diseases of bacterial origin has been observed, and it appears likely that the eye disease, xerophthalmia, which has hitherto been regarded [46] as one of the characteristic symptoms associated with a deficiency of fat-soluble A in the diet, is really due to infection by a micro-organism to which the normal well-nourished animal is practically immune. [47]

More definite results have been obtained by E. Mellanby [48] in some experiments on dogs. He found that puppies fed on a diet deficient in fat-soluble A rapidly developed typical rickets. The symptoms were speedily relieved by adding butter fat or cod-liver oil to the diet. Contrary to what had been observed in similar cases by other investiga-

[46] R. Guiral, *Rev. Med. y Cirugra*, Havana, 1919, **24**, 157 ; *Physiol. Abst.*, 1919, **4**, 224.

[47] E. C. Bulley, *Biochem. J.*, 1919, **13**, 103.   [48] *Lancet*, 1919, i, 407.

tors, Mellanby's puppies grew rapidly on the basal diet, but it appears likely that this growth is attributable to the small amount of fat-soluble A left in the diet. The author suggests that growth may occur in the absence of the vitamine, but it is pathological instead of normal growth. In any case, the results substantiate the view that it is exceedingly important that young children should be supplied with an ample supply of this vitamine.

A discovery with immediate practical bearings has recently been made by S. S. Zilva [49] in this field of investigation. He has found that the fat-soluble A in butter and milk is destroyed by exposure for 8 hours to ultra-violet rays. Since cow's milk is sterilised on a commercial scale by exposure to these rays, it seems likely that this treatment may cause a considerable reduction in the nutritive value of the milk. These rays do not exert any injurious action on the antineuritic and antiscorbutic vitamines.

Water-Soluble B.

Examination of certain cereals indicates that the antineuritic or water-soluble B vitamine is situated for the most part either in the embryo or the outer layers of the endosperm. Apparently in the plant itself, vitamines are associated with active growth, and it may be that the plant cells actually require vitamines in order to carry out certain life processes.[50] The presence of vitamine in the embryo and outer layers of the grains of cereals suggests that, from the physiological standpoint, brown bread is to be preferred to white; and this conclusion has been confirmed [51] by experiments on fowls in which polyneuritis was produced by prolonged feeding with white, but not by feeding with brown bread. Although the function of this vitamine has not been discovered, some striking differences have been observed [52] in the content of enzymes in the tissues of polyneuritic and normal animals respectively. The amount of catalase in the tissues of pigeons is stated to be lower to the extent of 44% in avian polyneuritis as compared with that present in normal birds. A corresponding decrease has been noted [53] in the amount of diastase in the blood. On the administration of extracts containing the missing vitamine, the diastatic content of the blood increases at the same rate as improvement occurs in the condition of the bird. It has been suggested that this vitamine directly or indirectly stimulates the oxidation processes occurring in the body. Voegtlin and Myers [54] express the view that this vitamine

[49] Biochem. J., 1919, 13, 164; J., 1919, 693A.

[50] C. Voegtlin and C. N. Myers, Amer. J. Physiol., 1919, 48, 504.

[51] C. Eijkman and D. J. H Pol, Proc. Akad. Sci. Amsterdam, 1918, 21, 48, Physiol. Abst., 1919, 4, 176.

[52] R. A. Dutcher, J. Biol. Chem., 1918, 36, 63; Physiol. Abst., 1918, 3, 520.

[53] S. Fuji, Jikwa Zasshi, 1917, 203, 36 : Physiol. Abst., 1918, 3, 520.

[54] Proc. Amer. Physiol. Soc., Amer. J. Physiol., 1919, 49, 124; Physiol. Abst. 1919, 4, 334.

is closely related to, if not identical with secretin, because acid extracts of duodenal mucous membrane containing secretin have been found to relieve avian polyneuritis and, vice versâ, extracts of yeast containing the antineuritic vitamine on injection into the blood cause marked pancreatic secretion and bile flow.

Water-Soluble C.

A considerable amount of attention has been given to this vitamine, especially by the workers at the Lister Institute of Preventive Medicine. Although many materials have been investigated, no richer source of this vitamine has been discovered than ordinary lemon juice. Lime juice is greatly inferior to lemon juice, and, in passing, it may be noted [55] that historical research has shown that the " lime juice " given to the sailors of the British Navy and mercantile marine to combat epidemics of scurvy which have occurred from time to time has always been made from lemons. Although fresh lime juice has a certain amount of antiscorbutic value, it is far inferior to fresh lemon juice, whilst preserved lime juice is useless. Swede juice has been found to be the most effective substitute for the juice of oranges and lemons, whilst the vitamine has also been recognised [56] in onions, turnips, tomatoes, potatoes, carrots, beetroots, and green vegetables generally. Clover and similar plants contain most vitamine when in the immature stage, which suggests that hay is more beneficial when it is cut before the grasses are fully grown. Preparations containing the antiscorbutic vitamine in a concentrated form can be obtained [57] from lemon or orange juices by removing the citric acid and then concentrating the clear liquid at a temperature not exceeding $10°$ C. By evaporation in a vacuum, an active dry residue can be obtained, whilst from apples [58] similar products containing a small proportion of water can be produced, which retain their activity for many months. After boiling orange juice, and making it slightly alkaline to litmus, it may be injected intravenously directly into the blood circulation with good effect. [59]

The antiscorbutic vitamine in cabbage [60] is destroyed by drying at $100°$ C. ; but if the desiccation is carried out at a low temperature, a preparation is obtained of small though definite antiscorbutic value.

[55] H. Chick, E. M. Hume, R. F. Skelton, and A. H. Smith, Lancet, 1918, ii, 735 ; J., 1919, 351R.

[56] T. B. Osborne and L. B. Mendel, J. Biol. Chem., 1919, 39, 29 ; J., 1919, 788A.

[57] A. Harden and S. S. Zilva, Biochem. J., 1918, 12, 259 ; Physiol. Abst., 1918, 3, 521.

[58] A. Harden and R. Robison, J. Roy. Army Med. Corps, 1919, 32, 48 ; Physiol. Abst., 1919, 4, 88.

[59] A. F. Hess and L. J. Unger, Proc. Soc. Exp. Biol. and Med., 1918, 15, 141 ; Physiol. Abst., 1918, 3, 522.

[60] M. H. Givens and B. Cohen, J. Biol. Chem., 1918, 36, 127 ; E. M. Delf and Tozer, Biochem. J., 1918, 12, 416 ; Physiol. Abst., 1919, 4, 13^

On storing, however, the antiscorbutic power rapidly disappears, and in three months the cabbage is entirely inactive. Raw tomatoes when included in the diet of the guinea-pig give efficient protection against scurvy,[61] and even after drying at.35° C. a certain proportion of the original antiscorbutic power is retained. Vegetables such as cabbages, carrots, etc., retain their antiscorbutic power when boiled in water for a short time, especially when taken young and fresh. Canned vegetables, with the exception of tomatoes, have only a small antiscorbutic value.

The results obtained by Chick and others referred to in the previous report showing the low antiscorbutic power of ordinary milk have since been amply confirmed and extended. Evidence has been brought forward [62] indicating that cow's milk has a higher antiscorbutic value in summer than in winter, due probably to the difference in diet, fresh herbage being consumed in the summer, and hay, oil cake, and roots in the winter. It is suggested that the use in winter of turnips or swedes rather than mangolds should lead to the production of a milk of higher antiscorbutic value. The results of the experimental work show conclusively that dried cow's milk is inferior to raw milk in antiscorbutic power, and that even raw cow's milk is a food of comparatively low value in this respect. It is most desirable, therefore, that extra antiscorbutic material should be provided when infants are to be nourished entirely on cow's milk, and for this purpose the raw juices of oranges, swedes, or tomatoes are specially recommended. In the case of the last named, good results have been obtained even with the tinned material.[63]

The study of the increase in antiscorbutic vitamine during the germination of seeds has yielded particularly interesting results.[64] The antiscorbutic value of dried peas and lentils after soaking in water for 24 hours followed by germination for 48 hours at room temperature is five to sixfold that of the dry seeds. Although inferior to orange or lemon juice, cabbage, or swedes, germinated cereals are equal in antiscorbutic value to many other vegetables such as potatoes, carrots, or beetroots. A considerable proportion of the antiscurvy power generated in these germinated seeds may be destroyed at the boiling temperature so that the cooking should be for as short a time as possible. Several interesting instances illustrating the antiscorbutic value of germinated seeds might be given. In a hospital [65] for Serbian soldiers,

[61] M. H. Givens and H. B. McClugage, J. Biol. Chem., 1919, 37, 253; Physiol. Abst., 1919, 4, 133.

[62] R. E. Barnes and E. M. Hume, Biochem. J., 1919, 13, 306.

[63] A. F. Hess and L. J. Unger, Proc. Soc. Exp. Biol. and Med., 1918, 16, 1; Physiol. Abst., 1919, 4, 30.

[64] H. Chick and E. M. Delf, Biochem. J., 1919, 13, 199.

[65] H. W. Wiltshire, Lancet, 1918, ii, 811.

as many cures of scurvy were obtained by treatment with germinating haricot beans as with fresh lemon juice. Another illustration [66] is afforded by the results of an inquiry into the cause of an outbreak of scurvy among a Kaffir battalion in France. The diet of this community was arranged so as to reproduce as nearly as possible that of the native kraals, where, in spite of a limited diet, scurvy is unknown. The arrangements even included the provision of a native beer brewed from millet, of which large quantities are regularly consumed in Africa. When the outbreak of scurvy occurred a court of inquiry was held, and the following fact was established, viz. that the beer as brewed in South Africa was prepared from germinated millet, but that in France the process of germination had been omitted for reasons of convenience.

The symptoms of scurvy in guinea-pigs, and particularly the degenerative tooth changes, have been investigated and described at length by S. S. Zilva and F. M. Wells.[67] The disease is identical with that occurring in the human subject, and it is suggested that the prevalence of tooth decay in man may be in part due to the occurrence of slight but unrecognised attacks of scurvy. Similar results have been obtained by M. Mellanby on dogs,[68] and by A. Harden and S. S. Zilva [69] and R. E. Barnes and E. M. Hume [62] on monkeys.

Pellagra.

The results of several investigations have recently been published [70] dealing with the œtiology of this disease. In South Carolina practically all the new cases of pellagra in the community have been found to develop whilst the persons were residing in the same house with or next door to a pellagrin in the active stage of the disease, or within six months after such an exposure to the disease. It has been found also that following the installation of a proper sewage system the spread of the disease has been almost completely arrested. The general bulk of the evidence indicates clearly that this disease is not due to the lack of a specific substance such as is without question responsible for beri-beri, and it is probable that the observed connection between pellagra and a diet of maize is due only indirectly to the poor state of health thereby produced rendering the person concerned more liable to the attack of an unknown specific " pellagra " bacillus.

Cᴀᴛᴛʟᴇ Fᴏᴏᴅs.

Much attention has been given to the possibility of treating straw with acid or alkali, or with steam under pressure, to render it a more

[66] H. W. Dyke, *Lancet*, **1918**, ii, 513.
[67] *Proc. Roy. Soc.*, 1919, **90**ʙ, 505; *Physiol. Abst.*, 1919, **4,** 178.
[68] *Lancet*, 1918, ii, 767.
[69] *J. Pathol. and Bact.*, 1919, **22,** 246; *Physiol. Abst.*, 1919, **4,** 274.
[70] *Med. J. Birmingham*, 1918, **11,** 786; *Physiol. Abst.*, 1919, **4,** 224.

suitable food for cattle. By treatment with acid [71] a considerable proportion of insoluble material can be converted into sugar-like products. By treatment with alkali [72] the straw appears to be modified in quite a different manner. The fat or wax and most of the silica are removed, and the residual straw is brought into a soft condition most favourable for assimilation by ruminant animals. By this process, however, a small loss of soluble matter is involved owing to the necessity of removing and washing out the excess of alkali.

Castor bean meal,[73] palm-kernel cake,[74] lupins,[75] seaweed,[76] fish-meal,[77] brake fern,[78] and horse-chestnuts [79] can all be made to furnish more or less suitable foods for cattle. Freshly pressed castor-oil cake contains the highly toxic substance, ricin, but by submitting the material to a high temperature, the ricin is completely destroyed, and the cake converted into a satisfactory cattle food. Palm-kernel cake is a profitable cattle food, provided it is in a dry state. In the presence of traces of moisture it rapidly becomes rancid, with the production of an intense odour of sweat due to the liberation of caprylic acid. Under good conditions, however, it can be kept for many months without any unsatisfactory changes developing. Lupins must be extracted with water to remove the poisonous alkaloid, before being employed for cattle feeding. Even then they are not easily digested and should be mixed with finely chopped oat straw before being given to the animals.

Fish-meal is made from fresh offal recovered from fish at the ports, together with whole fish rejected as unfit for human consumption, or unsaleable owing to an excessive supply. The raw material is steamed and a portion of the oil removed by pressure. The residue is then completely dried and crushed to a meal. It is said to be an excellent cattle food.

[71] A. Jonscher, Z. offentl. Chem., 1918, 24, 279; J., 1919, 301A. F. Honcamp and E. Blanck, Landw. Versuchs-Stat., 1919, 93, 175; J., 1919, 841A.

[72] F. Hansen, Biedermann's Zentr., 1919, 48, 110; J., 1919, 435A.

[73] Anon., J. Board Agric., 1918, 24, 1444.

[74] J. R. Furlong, J. Agric. Sci., 1919, 9, 137; J., 1919, 384A.

[75] Boodt, Tydsch. der Neder. Heidemaatschappij, 1918, 30, 68; Physiol. Abst., 1919, 4, 285.

[76] B. R. de Bruyn, De Veldbode, 1918, 807, 524; Physiol. Abst., 1919, 4, 285.

[77] C. Crowther, J. Bd. Agric., 1919, 26, 480; J., 1919, 735A.

[78] A. Zlataroff, Z. Nahr. Genussm., 1918, 35, 483; J., 1918, 712A.

[79] A. Heiduschka, Pharm. Zentralh., 1918, 59, 291; J., 1919, 49A.

WATER AND SEWAGE PURIFICATION.

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It is impossible to say for a given year how much it has borrowed from the wisdom and experience of previous years, or to try to measure its influence on the years that are to come. Even present-day tangible discoveries may show, to the far-seeing eye, some of the honourable rust of antiquity, and indeed the extent to which we borrow on the past in thought and deed is incapable of measurement. Thus it happens that in trying to sum up the knowledge gained in a particular year we are always trespassing on the past and, conversely, we may be doing the year in question too little credit in relation to its bearing on future progress. Nevertheless, it is desirable to attempt periodically to take stock of current knowledge, to endeavour to show the general trend of events, and to indicate some of the directions in which future progress is likely to, or should, take place.

The year 1919 has been a culminating one in the struggle of expediency over sentimentality, and in new ways of looking at things. Some of the events, which during recent years have brought us to-day to this new jumping-off ground for more rapid progress, may be briefly described.

WATER.

At the very outset of the war, the pioneer work on chlorine sterilisation at Lincoln [1] in 1905 bore full fruit. Giving full credit to all other preventive agencies at work, it may still be said that the health (thanks to Horrocks and his colleagues) of our Armies in the Field all over the world was considerably, if not largely, influenced by efficient chlorine sterilisation processes.

In 1915 a notable event occurred—Aberdeen [2] received the assent

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[1] *Fifth Report of the Royal Commission on Sewage Disposal, Appendix IV.* pp. 99–166; also pp. 84–98; also 171. Dr. Reece's *Report to the Local Government Board on Lincoln epidemic* (No. 226), 1906.

[2] *Private Legislation Procedure (Scotland) Act,* 1899. *Aberdeen Corporation Water Provisional Order, Proceedings at Inquiry,* October 21–27, 1915 (The University Press, Aberdeen).

of Parliament to a scheme for purifying the River Dee for waterworks purposes by (1) excess-liming, (2) short storage, and (3) rapid filtration, the saving in capital cost on alternative schemes exceeding £100,000. The way towards this event was paved by the discovery that caustic lime present in water, in even the smallest excess, exercised a strong bactericidal action.[3]

In 1916 the Metropolitan Water Board[4] decided to save coal by chlorinating raw Thames River water (70–80 million gallons a day) and allowing the treated water to flow by gravity down the Staines Aque-duct, instead of first pumping it up into Staines Reservoirs. The difference between the cost of pumping and the cost of chlorinating is about £1000 a month. The treatment is in successful operation to-day.

The New River supply[5] of the Metropolitan Water Board is made up of a variable mixture of New River water (Upper Lea water) and pure well water. During the greater part of the year, owing to the good quality of the well water and the relatively satisfactory state of the river water, the filtered water results are remarkably good, as judged by the ordinary chemical and bacteriological standards, despite the fact that the rate of filtration at the New River works is considerably in excess of that practised at the other works of the Board. During winter floods, the river water deteriorates so much that the excellent quality of the well water fails to " mask " the deterioration of the mixed filtered water product. The storage reservoirs at Hornsey and Stoke Newing-ton are far too small to affect the position materially. In 1916 the Metropolitan Water Board started investigations with the object of seeing whether it might not be possible to remedy this state of affairs by chlorination. It is obvious that to increase materially the filtra-tion area, or to provide adequate storage accommodation, would mean an immense capital outlay in order to improve matters during these transitory periods of deterioration.

The experiments have been most satisfactory in a bacteriological sense, but the unfortunate fact remains that when the treatment was carried out uninterruptedly for longer than about a fortnight, the water acquired a decidedly objectionable taste. This was partly due to the filters gradually and progressively adsorbing taste-imparting materials, which eventually escaped into the filtered water, so that even when the treatment was perforce stopped the taste remained for some time in

    [3] *Metropolitan Water Board, Director of Water Examination's Eighth Research Report* (see also Ninth and Tenth Research Reports).
    [4] *Metropolitan Water Board, Director of Water Examination's Twelfth Research Report* (see also Eleventh, Twelfth, and Thirteenth Annual Reports).
    [5] *Metropolitan Water Board, Director of Water Examination's Eleventh, Twelfth, and Thirteenth Annual Reports.*

the water as supplied to consumers. It should perhaps be explained that for technical reasons it was impossible to chlorinate the water subsequent to filtration. Although a filtered water may require less chlorine for sterilisation purposes than an unfiltered one, the writer's experience has been that with some waters, at all events, there is a greater liability to taste troubles if the chlorine is applied subsequent to the filtration process. In 1918 a system of super-chlorination and de-chlorination was adopted, it having been found in the laboratory that even a grossly-super-chlorinated water had no taste after de-chlorination. In practice, however, the results were only moderately successful with regard to absence of taste, although yielding excellent results bacteriologically, nevertheless it did seem as if the kind of taste was considerably modified in character by this method of treatment. The matter is being further investigated, and it is hoped that some satisfactory solution of the difficulty may yet be found. The writer has recently discovered that potassium permanganate in doses of 2 8 lb. per million gallons is most effective in preventing or removing the taste of chlorinated waters whether added before, simultaneously with, or after the chlorine. It appears, however, to be ineffective if the permanganate is added before, and the chlorine after filtration, although the converse plan yields successful results, as does also their joint use either before or after filtration. Sodium manganate may be used successfully instead of permanganate of potassium. The matter has gone beyond mere laboratory experiments. For example, 33 million gallons per day flowing down an open channel were treated with chlorine (1 in 1 million). The water a little way below the point of treatment (about ¼ hour's flow) had, after de-chlorination, a decided " chemist's shop flavour " or " iodoform " taste. Next potassium permanganate (8 lb. per million gallons) was added immediately below the point at which the chlorine entered the water. After a suitable interval it was again, after de-chlorination, tested at the same spot as before, and it no longer gave any taste. The experiment was repeated twice more with exactly the same satisfactory results. By this " see-saw " experiment it was proved conclusively that permanganate under practical out-door conditions can prevent or remove the objectionable taste of, at all events, some chlorinated waters. With a longer contact the dose of permanganate may sometimes be reduced four times. The point that the writer desires to emphasise is that the New River experiments constituted an attempt to tide over economically periods of crisis, and it is difficult to say how far such efforts may eventually lead us. For example, speaking more particularly of river-derived water supplies, there are normally two periods of the year when the filtered water results are apt to be relatively unsatisfactory. In summer, during very hot weather, the consumption of water may be so materially

increased as to lead to considerably increased rates of filtration, and in the winter the water about to be filtered may be much less pure than the normal, and, in addition, there are a variety of circumstances which increase the difficulties—for example, the rate of filtration may have to be increased during exceptionally cold weather, owing to increased consumption of water consequent upon burst pipes and taps left running overnight. Further, frosty weather may lead to mechanical interference with the filtration process, and a seasonal deficiency in the water of those growths which form a skin on the surface of the sand in the filter may also be a factor in influencing the results. It is at times such as these that sterilisation processes seem specially attractive, for the interest on the capital cost and the working costs are inconsiderable, or, at all events, immeasurably small, in comparison with the alternative of an increase of filtration area not really needed except in periods of stress. Developments in the foregoing direction seem likely to attract considerable notice in the near future. There is also the point that consequent upon the war all engineering projects have been greatly delayed and that a considerable time must elapse before new works can be completed. Meanwhile, the consumption of water may be progressively increasing, leading to increased rates of filtration and to a worse water being supplied to consumers. Here again chlorination as a temporary measure may be found extremely useful.

In 1917 Rotherham decided on the policy of re-using the abandoned and severely censured Ulley gathering ground, and, subject to the approval of the Local Government Board, to supply water from this source, after being rendered safe by sterilisation processes, to the inhabitants of that town.

Somewhat later, Cardiff[6] determined to adopt a similar course in regard to a portion of their gathering ground, which had been provisionally given up as not wholly satisfactory for waterworks purposes.

The saving involved if these two decisions could be successfully carried out was of a very material kind.

In 1917 Accra was faced with a very unsatisfactory position as regards its water supply. The water (swamp water, liable to pollution) deteriorated to a remarkable extent in the relatively large storage reservoirs, absolutely necessary for purposes of quantity. Exhaustive experiments were made, and it was found that by applying the " excess lime " method of treatment the water was freed from excremental bacteria (e.g., B. coli) and remained clear, odourless, and free from

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[6] C. H. Priestley, " Temporary Sources of Supply in Times of Emergency," Water, July, 1919, p. 175.

growths under conditions of storage. The saving on alternative purification works represented a large sum of money. This is the first occasion on which the excess-lime method has been used for the express double purpose of destroying " plankton " development and rendering water safe from the epidemiological point of view.

In the present year Sheffield[7] conceived a scheme for the utilisation of river water as compensation water, which, despite its bold and unprecedented character, received, with certain reservations, the assent of Parliament. ' It is of interest to consider this unique proposal at some length, because its influence on future procedures may be far-reaching. Sheffield was obliged by Act of Parliament to pass about 10 million gallons daily of pure moorland water from the Dam-Flask and Rivelin reservoirs. down the course of the grossly polluted river Don (which, of course, was not used for drinking purposes) as compensation water. The proposal was to reserve this pure water to increase the domestic supply to Sheffield and to abstract from the Don below the point where the sewage effluent from the city, together with many other impurities, entered the river an approximately similar amount of water, to purify and soften it, and to pump the purified river water back about eleven miles up-stream and pass it through the statutory mill gauge in lieu of the unnecessarily pure water discharged from the reservoirs for compensation purposes. The word " unnecessarily " in this connection is used advisedly, for the river Don water was only used for trade purposes and was so heavily polluted with ochre streams, trade effluents, and waste liquors near and below the point of discharge of the compensation water that to " feed " it with water of a high degree of purity was a wasteful procedure.

Sheffield considered that if they purified and softened the river water abstracted below Sheffield to a standard at least equal to that proposed by the Royal Commission on Sewage Disposal, and softened it as well, they were in no way injuring trade interests, destroying the amenities of the district, or endangering health. Indeed, by utilising a pure moorland water for augmenting the domestic supply of Sheffield, they were greatly contributing to the prosperity and welfare of that important city, and conserving the water and financial resources of the country, inasmuch as any alternative project for providing an equal quantity of potable water would have 'involved the ratepayers in a capital outlay of approximately 3 million pounds, compared with £350,000.

The proposed method of purification was by lime and soda treatment, followed by efficient filtration.

In proof of ability to purify the water efficiently an experimental plant was erected and elaborate tests made. The following table shows some of the results obtained :

[7] *Sheffield Corporation's Bill* (1919), *Part II.—Waterworks.*

	Analyses of River Don water taken at proposed intake. Parts per 100,000.	Analyses of river water after treatment. Parts per 100,000.
Solids in suspension . . .	Nil to 10·00	Nil
Hardness	10·35 to 30·50	3·71 to 8·71
Oxygen absorbed in 4 hours .	0·32 to 2·38	0·19 to 0·80
Acidity	Nil	—
Total alkalinity.	—	5·00 to 8·25
Chlorine	2·00 to 21·60	2·00 to 21·00

It may be said that Parliament endorsed the wise proposals of Sheffield on all points of principle, but imposed certain reservations and modifications, as a measure of precaution, in view, no doubt, of the unique and unprecedented nature of the project.

Briefly these were as follows :

1. The maximum quantity of water which may be abstracted from the River Don and pumped back for use as compensation water is roundly 5 million gallons per day.

2. The treated water is to be discharged with at least an equal quantity of reservoir water subject to an addition of 10% in the quantity of treated water.

3. The standard of purity and the terms and conditions prescribed by the Act may be varied by the Ministry of Health on the representation of the Corporation, the West Riding Rivers Board, the Associated Millowners, or any other body or person having a substantial interest in the matter, after the expiration of four years from the date when the treated water is first used for Compensation purposes.

4. Prescribed standard : Solids in suspension, 2 parts per 100,000 ; hardness $CaCO_3$ (soap solution), 8 parts ; oxygen absorbed from $N/80$ potassium permanganate, in 4 hours, at 80° F., 1 part per 100,000, or on the average of 3 consecutive days not more than 0·75 part.

The Report of the Select Committee on Local Legislation which considered the Sheffield Bill stated :

" The Sheffield Corporation Bill contained entirely novel proposals with regard to water supply. The Corporation were allowed, after full evidence being given, to substitute for compensation water, which they are now under statutory obligation to discharge into certain rivers, an effluent from their sewage works purified to a standard required by the Bill, and which standard is based to a considerable extent on the findings of a Royal Commission of some years ago. The urgent need for, and difficulty in obtaining, a further supply of water for domestic purposes, combined with the special circumstances affecting Sheffield, make this case suitable for testing an experiment, which, if as successful as the evidence suggested, would be of incalculable advantage in other cases, where suitable conditions exist for its application."

In the preparation of these notes the writer is greatly indebted to the courtesy of Mr. Terry.

Within the last few years a great deal of attention has been directed to the suspended matters[8] (particularly the " plankton "[9]) in river and reservoir waters, owing to their effect in choking sand filters and sometimes in giving the water an offensive taste. At the Metropolitan Water Board's Laboratories it is the practice to examine bi-weekly all the samples of pre-filtration water (20–25 in number), river water, all the stored waters, gravel water, etc. The methods adopted are as follows :

The " resistance to filtration " (by this is meant the degree to which the suspended matters—living and dead—in a water interfere with its filtration) is tested in the following manner : A piece of linen of superfine quality (96 meshes to the linear inch) is folded four times, moistened with water and tied round the end of a glass tube ($\frac{1}{4}$ in. diameter) by means of a rubber band. It might be conjectured that a layer of sand would ·be more suitable than linen. The writer has tried it, and it gives a most disappointing range of results, unlike linen, when the results vary from 0·0 to over 300 according to the amount of suspended matter in the water. The tube is passed through a rubber bung which is fitted into a filtering flask, connected with a filter pump. The other projecting end of the glass tube has a piece of rubber tubing attached to it, and into this is inserted the end of a pipette containing 100 c.c. of the sample of water to be examined. The water passes through the linen into the flask, and practically all the suspended matter is retained on the inside of the linen. The rubber bung and glass tube are then detached and fitted on to the additional piece of apparatus.

This is merely a convenient arrangement for supplying tap water under a constant head (about 5 ft.). The water is filtered through the linen, with its skin of suspended matter derived from 100 c.c. of the original water, for the space of one minute, and the filtrate is then measured. A water having little or no suspended matter will, in these circumstances, give a filtrate of, say, 200-300 c.c.[8,9] A water badly affected with algal growths may yield no measurable filtrate, and between these two extremes all kinds of results are obtained (see charts pp. 472–3).

As regards the microscopical appearances of the suspended matters, the following photographic method of examination is used in order to obtain qualitative and quantitative pictures of the condition of the

[8] On pp. 35 and 37 of " *Studies in Water Supply* " (Messrs. John Bale, Sons & Danielsson, Ltd.) diagrams will be found fully illustrating the methods employed. See also *Metropolitan Water Board, Director of Water Examination's Twelfth Research Report*, and Ninth, Tenth, Eleventh, Twelfth, and Thirteenth Annual Reports.

[9] Photomicrographic illustrations of the various growths in water will be found in " *Studies in Water Supply* " (Messrs. Macmillan & Co.), " *Rivers as Sources of Water Supply* " and " *Rural Water Supplies and Their Purification* " (Messrs. John Bale, Sons & Danielsson, Ltd.), and also in the *Director of Water Examination's Reports to the Metropolitan Water Board*.

RESISTANCE TO FILTRATION EXPERIMENTS.

Number of c.c. filtered per minute.
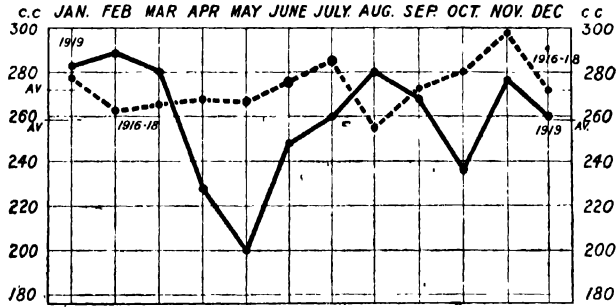
S AND V. WALTON STORED WATER.
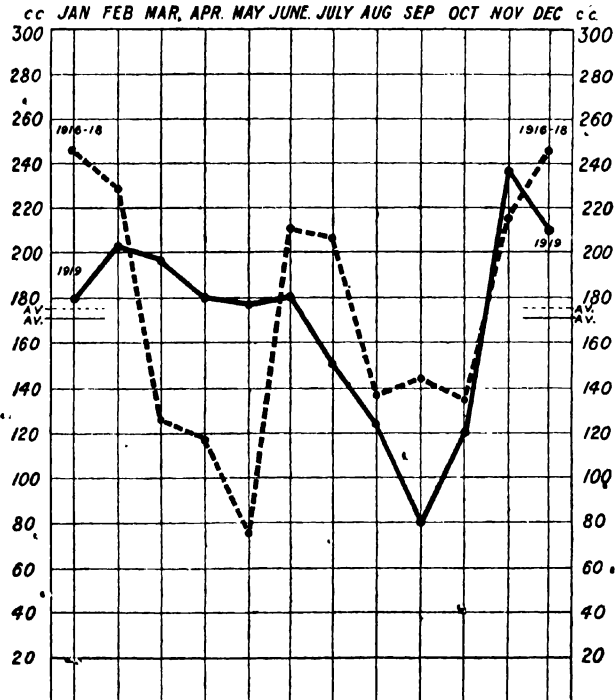
WEST MIDDLESEX No. 1. RESERVOIR STORED WATER.

RAW THAMES WATER
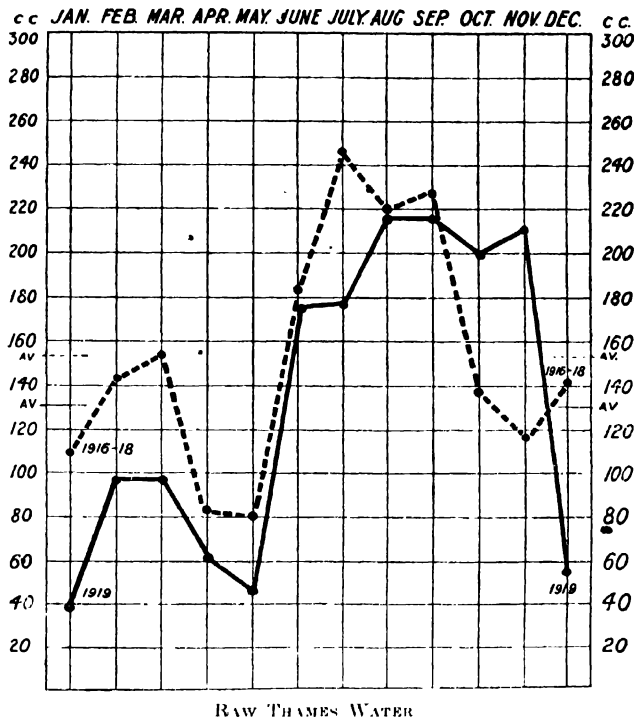
various waters : 20 c.c. of the water are placed in a glass tube and centrifuged, the result being that all matters in suspension are driven to the bottom of the tube. The contents are then carefully poured off to a little above the 0·2 c.c. top mark on the narrower portion of the tube. The pipette is then used to suck out the water to exactly the level of the 0·2 c.c. top mark, care being taken not to disturb the sediment. This water is expelled from the pipette, which latter is then used to mix thoroughly the deposit with the water remaining in the tube. Between the two marks is exactly 0·1 c.c., and this amount, or one-half of the whole of the suspended matter in 20 c.c. of water, is transferred with the pipette to the small cell. A trace of formalin is added to prevent the movement of any motile organisms that may be present, and now we have 0·1 c.c. or the suspended matter pertaining to 10 c.c. of water, lying in the cell ready to be photographed.[8, 9] The slide is next centred, so that the middle of the cell lies exactly below the centre of the lens. A magnification of 50 diameters is employed

[8, 9] See footnotes on page 471.

as this, in most cases, is quite large ˙enough for diagnostic purposes, and it gives a reasonably flat and a relatively large field. Of course, the whole of the 0·1 c.c. is not photographed, but it has been found experimentally that about one-twentieth part appears in the picture, which corresponds to the suspended matter in ½ c.c. of the original water (see plate illustrating some of the growths found in water).

The river water usually filters badly in winter, due to the mud, silt, and dirt brought down by the floods, relatively badly in spring and early summer, due to growths (*e.g.*, *synedra*, *pleurosigma*, *diatoma navicula*, *tabellaria*, etc.), but for the remainder of the year the results are usually satisfactory.

The stored reservoir water varies enormously, some reservoirs yielding excellent water all the year round, whilst in other cases the results deteriorate, due to an over-development of growths in the late winter and early spring, and again perhaps in the summer and early autumn months. The growths in the reservoir water are usually different from those commonly present in the river water, are much more abundant and of more varied character (*e.g.*, *fragilaria*, *asterionella*, *tabellaria*, *pandorina*, *cyclotella*, *stephanodiscus*, *ceratium*, *glenodinium*, *synura*, *staurastrum*, *pediastrum*, *scenedesmus*, *eudorina*, *volvox*, *oscillaria*, etc.). In the absence of any over-development of these growths, stored water filters much better than river water. The further study of the conditions which foster the development of these growths is highly important, as they sometimes give water a most objectionable taste and smell, and, apart from this, their choking effect on filters is often a serious matter. The choking effect may actually lead to a shortage of available water and interfere so markedly with the normal working of the filters that an impure water may be supplied to consumers.

As regards remedial measures, copper sulphate, in doses of 1 in 1 to 1 in 5 millions. has been found to be most effective, especially if applied at ˉan early stage of " plankton " development ; and potassium permanganate (dose 5 lb. per million gallons) has a remarkable influence in removing the objectionable taste produced by excessive development of undesirable growths in water.

Despite the extension of rapid filtration plants, the advocates of the slow sand filters remain, rightly or wrongly, absolutely unshaken in their belief in the advantages of this well-tried method of purification. The question, however, which is at present receiving considerable attention is this : Is it permissible with, possibly even without, the use of aluminium sulphate as a coagulant to filter at an exceedingly rapid rate, to condone any falling-off in the chemical results, and to secure the safety of the consumer by a post-filtration chlorination pro-
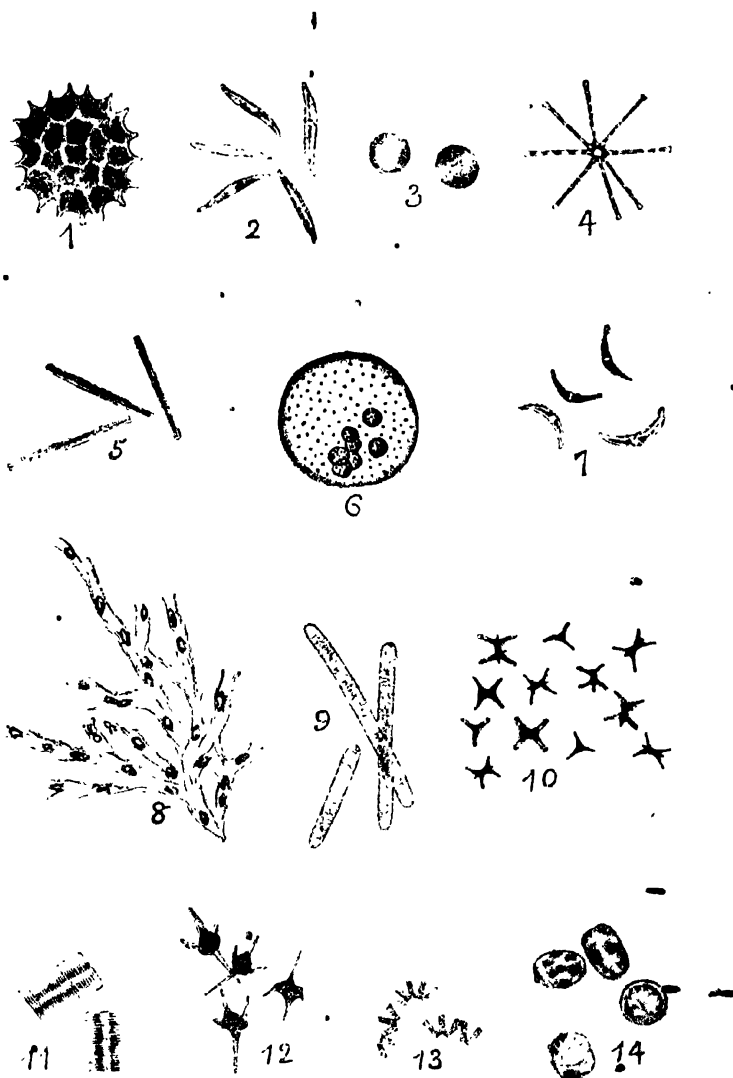
1. *Pediastrum* × 400. 2. *Pleurosigma* × 50. 3. *Glenodinium* × 150.
4. *Asterionella* × 150. 5. *Synedra* × 50. 6. *Volvox* × about 25. 7. *Closterium* × 50.
8. *Dinobryon* × 180. 9. *Oscillaria* × 250. 10. *Staurastrum* × 50. 11. *Fragilaria* × 50.
12. *Ceratium* × 50. 13. *Tabellaria* × 50. 14. *Cyclotella—Stephanodiscus* group × 400.

GROWTHS FOUND IN RIVER AND STORED WATER,

cess ? [10] There are many things 'which might be urged against such a procedure, but it is, at all events, attractive on economical grounds, and the final sterilisation process, if properly carried out, would ensure epidemiological safety.

The writer has had so much occasion to deal with the question of accident [11] in connection with waterworks procedure that he approaches the subject with some diffidence. Yet it is a matter of such importance, and has been, and is being, so seriously neglected that the time seems opportune, despite the, perhaps unduly, tolerant and non-critical attitude adopted by the writer in this article, to utter a word of grave warning. It is extremely difficult to define accident in the sense here suggested. The epidemiologist, bacteriologist, expert in preventive medicine, and men of special knowledge in these matters are so fully aware of the significance of this subject that no words of explanation are needed. Outside certain circles there is room for elucidation. In its simplest form it is obvious that to allow the possibility of any adventitious water to enter a water supply subsequent to its purification is fraught with potential danger, and danger which even the most astute expert may be powerless to gauge. If filter beds, filter wells, culverts, service reservoirs, etc., are not watertight, it may be impossible for the trained observer to judge underground sources of pollution in other than a spirit of pure speculation. It might be surmised that, in view of these difficulties, the watertight integrity of waterworks would be taken for granted ; failure indeed in this respect might be regarded as the senseless sacrifice, at all events in a potential sense, of all the money expended on purification. History, however, does not confirm this supposition, nor does experience even show that contaminations of most doubtful origin are absolutely foreign to the final stage of delivery of a reputedly safe water to the consumer. The fact is that waterworks authorities, having purified water to a high standard, are sometimes curiously oblivious to the circumstance that between their purification processes and the mouth of the consumer there may be a gap of dangerous significance.

The writer knew of a case where a shed had actually been constructed (it has since been demolished) over the top of a filtered water well, and was used by numerous workmen as a shelter and storage place for their tools. The only protection was that the mouth of the well was covered over with loose iron plates.

[10] *Metropolitan Water Board, Director of Water Examination's Thirteenth Annual Report.*

[11] See p. 104, " *Studies in Water Supply* " (Messrs. Macmillan & Co.) ; also p. 59, " *Rural Water Supplies and Their Purification* " (Messrs. John Bale, Sons & Danielsson, Ltd.) ; also heading " Accidental Contamination," Index to *Director of Water Examination's Research Reports* (*Metropolitan Water Board*) to be found at end of Eleventh Report on Research Work ; also his Second Annual and succeeding Reports.

Another case within his recollection' was one in which a 12-inch iron pipe, jointed in the middle, conveyed unfiltered and polluted water, used for condensing purposes, over the mouth of a filtered water well. One day a fracture occurred at the joint and a large volume of contaminated water was swept into the supply.

Yet another case presents itself. A consumer used the ordinary water supply at one part of an hydraulic press and a very impure high-pressure water at another part. A leaky piston allowed the impure water to displace the pure water in the supply pipes and probably in the main itself. The result was that a foul-tasting and polluted water was drawn from any pure water tap in the building.

There are many persons who believe that no water-borne, or milk, or food epidemic has ever resulted except as the result of an accident, and these observers explain the comparatively frequent non-occurrence of disease in connection with known pollutions by the absence of some accidental circumstance, which can convert a contamination of relatively small volume into an agency of incalculable danger (i.e., a change from non-specific to specific pollution). Concrete instances may be given. A water supply may be contaminated with matters of excremental origin, but none of the individuals contributing to the pollution may be suffering from disease, or the effects of disease. Imagine now that one of these individuals is suffering from typhoid fever, or cholera, or having suffered from these maladies is in the unfortunate position of being a typhoid or cholera " carrier." Such a person has unhappily become a " human factory of disease," and may contribute to any pollution myriads of typhoid or cholera germs. Immediately the whole aspect of affairs is changed, and what was previously a potential danger becomes at once a most dangerous menace, and in all probability the genesis of a widespread epidemic. Again, let us take the case of a dairy, in which the milkers are of unclean habits. No harm may result until perhaps one of the milkers contracts typhoid fever and returns to work as a typhoid carrier, in which event the safety of the milk consumers hangs on so delicate a thread as to be practically non-existent. One could give innumerable instances in support of these contentions, but enough has been said to show the peril surrounding the conduct of a waterworks undertaking if this question of accident is not kept prominently in the foreground.

Many things have to be considered—the health of workmen, sanitary conveniences on the works and their surroundings, questions of fishing, position of drains, cesspools, etc., watertight character of the whole system of supply (filters, culverts, filter-bed wells, service reservoirs, etc.), penalties attached to nuisance. undesirability of strangers being admitted to any part of the works (from source to consumer), possibilities of contamination of the filtered water in the engine wells, " insuction " into mains owing to diminished pressure, etc., etc.

The writer has had much experience in these matters, and he has seen great fluctuations in the quality of water, as judged by ordinary standards, supplied to consumers, without any serious result. Why should no harm necessarily result under conditions of obvious deterioration ? The answer is—because of the fortuitous absence of specific pollution. Is the position then always safe, if the ordinary analytical data are favourable ? The answer unfortunately is—no, if a new factor has arisen, namely, specific pollution, introduced probably by accident, and it is to be feared also in too many cases by avoidable accident. The contamination may be infinitely small in volume and yet almost inconceivably dangerous owing to its specific taint.

The lesson to be learnt is plain and insistent. The expert, with all his life-long knowledge of pollutions, specific and apparently non-specific, refuses to take any risks, which are foreign to a properly conducted and controlled waterworks undertaking. It remains for others to accept or reject advice based on experience, and, if the latter course be chosen, to accept full responsibility for so doing.

It may be said—what has all this to do with the year 1919 ? From the consumer's point of view, it has everything to do with 1920 and succeeding years, whether the lesson of avoiding accident is learnt now and security attained as a consequence, or ignored and a policy of danger persisted upon.

Before passing on to the question of sewage purification, the writer feels that some mention should be made of the mechanical " drifting sand " filtration plant at Toronto. Toronto is splendidly equipped for carrying out important water investigations. There are not only central Public Health Laboratories under the able directorship of Professor Nasmith, but filtration laboratories under the capable and experienced direction of Mr. Norman J. Howard. A very large number of samples are examined and many valuable researches carried out on water purification, and one can only compare the scale of their operations to that of the Metropolitan Water Board, which have always interpreted Section 25 of the Metropolis Water Act (1902) in the most liberal and imperial spirit, as if indeed their responsibility to humanity was of general and not merely of local significance. Can quite the same be said of all our large water undertakings throughout the United Kingdom ? It is to be feared that this cannot be said, but the fault is not to be found with the Medical Officers of Health, analysts, chemists, and bacteriologists concerned, but rather with Waterworks Authorities who, too often, are content with the little rather than the more, and who do not always recognise that applied science has infinite possibilities, not only as regards safeguarding health, but in respect of saving unnecessary expenditure, and that these matters should be looked upon in a national and not a parochial spirit.

It is true, however, that in very many cases the water supply is so pure that numerous analyses and comprehensive investigations may seem to be uncalled for, and, no doubt, this has influenced waterworks policy in the past. Nevertheless, a great deal can be learnt from the study of even pure water, and there can be but few waterworks which possess no problems awaiting solution by the trained observer.

The water supply for the city of Toronto is drawn from Lake Ontario, which is apparently being polluted to a progressively increasing extent (62% increase within the last five years, as judged by the *B. coli* test). Here we have an example of what a scientifically controlled and uniformly exercised supervision can do in the way of warning. Continuity of records can alone achieve such results, and Toronto is to be congratulated on this enlightened policy as regards the work of water examination. The late Theodore Roosevelt is said to have remarked several years ago that the people of Canada and the United States should be sufficiently civilised to be able to get rid of their sewage in some other manner than by dumping it into their drinking water.

Two filtration systems are used—the slow sand and " rapid drifting sand " types, and in describing briefly the results obtained the writer draws all his information from two interesting papers by N. J. Howard.[12]

As regards the former (slow sand), excellent results were obtained in 1918. The average number of bacteria (agar at 37° C.) per c.c. in the raw water was 356·3, and in the filtered water 2·2 (reduction 99·1%). The average number of excremental bacteria (rebipelagar at 37° C.) per c.c. in the raw water was 26·5, and in the filtered water 0·25 (reduction 99%). The average indicated number of *B. coli* present in the raw water was 11·36 per c.c., whilst the filtered water contained 0·027 per c.c. The total percentage removal of the colon bacillus in the filtered water was 99·7.

The rate of filtration for the year was 3·27 million imperial gallons per acre per day. The total amount of water filtered was 11,470 million imperial gallons. The water is subjected to a final chlorination process before delivery to the consumers. The average daily consumption per capita was 128 imperial gallons. To those not familiar with Canada and the United States this figure is an amazing one. The abundant sources of supply, the intensely cold climate, the comparative non-control of waste, and many other factors influence the position. Yet, when a water, however illimitable in bulk quantity, has to be purified, it does seem at first sight that a curtailed consumption might be cheaper than increased purification works. On the other hand there is the fact that the purification of water forms but a small proportion of the total cost of a waterworks undertaking.

[12] " *Contract Record and Engineering Review* " (Toronto), **1919,** Sept. **17, No. 38,** p. **871 ;** No. **41,** Oct. **8, p. 937.**

The mechanical " drifting sand " filtration plant deals with 60 million gallons a day at a rate of 150 million gallons per acre per day (see fig. 2). The purification is brought about by the use of alum (average 1 grain per gallon) without previous sedimentation : " drifting sand," which is constantly being washed and automatically replaced (by patented devices) ; a stationary effective cone of sand, which is only back-washed and cleaned when the loss of head becomes a material factor ; and a final post-filtration chlorination process (0·2 part per million). The initial loss of head in the filters is 6 ft., and in the process of operation this gradually increases to 11 ft. when the filter is back-washed. The life of the filters ranges between one and seven days, according to the physical condition of the water being treated and the amount of coagulant being used. Is it permissible to con-clude, without being supercri-tical, that the advantages of the " drifting automatically washed and replaced sand " is, after all, only relative ? Wash-ing apparently takes 20 min-utes and then the filter is run to waste for another 20 minutes. Assuming that the washing is reasonably perfect and the final sterilisation process really effective, the waste of 20 min-utes' flow of water seems to be hardly warrantable, unless on the score of added security. The amount of dirty waste
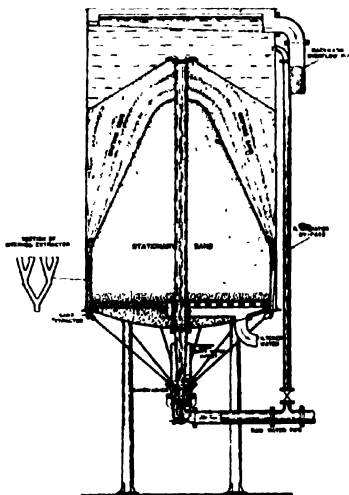
Fig. 2

water passing through the sand washer is stated to be 2%, whilst an additional 1–2% is used for backwashing and waste purposes. This is an appreciable proportion of the total supply, but when water is superabundant the matter becomes of small importance.

The dose of alum was on the average only 1·027 grains per gallon, but during periods of high pollution as much as 2·5 grains had to be applied.

Excluding three abnormal records, the bacteriological results were as follows :   The average numbers of bacteria (agar at 37° C.) per c.c. in the raw and filtered waters were 303·6 and 34·7 respectively (88·4% reduction).   The raw water contained 6·08 B. coli per 1 c.c., and the filtered water 0·22 per c.c. (96·4% reduction).   The chlorinated water showed an average bacterial count of 1·72 per c.c., whilst only two

H H

samples out of 1900 samples examined showed the presence of *B. coli* in 1 c.c. (99·9% reduction).

The writer cannot trace in Howard's interesting paper any precise reference to *B. coli* tests on 100 and 10 c.c. of liquid. It would be of interest to learn how far the filtration and chlorination processes removed *B. coli* from these amounts of water, because, obviously, it is one thing to get excellent results on a 1 c.c. basis and quite another thing to obtain similar " findings " when dealing with larger volumes of water.

A comparison of the results with those previously given would seem to show that the " drifting sand " filtration system did not, generally speaking, yield such good bacteriological results as the slow sand filtration process.

An interesting practical conclusion is revealed in the paper, namely, that experiments showed that the time element is apparently not of vital importance in the administration of the alum, that is, that there is no great, if any, advantage in allowing a long, if any, time to elapse between the addition of the alum to the water and the filtration process.

Race, an observer of rare merit, had previously obtained similar results at Ottawa.

It would be of interest to know Howard's opinion of the relative advantages of the two processes of treatment (slow sand and rapid drifting sand), and how they compare with each other when judged on engineering and financial grounds ; and also how the latter compares with other types of rapid filters. The writer has had ample experience of the working of all the well-known rapid filters used in this country, but cannot speak from personal knowledge as regards the rapid " drifting sand " filters.

SEWAGE.

Progress in sewage purification has been necessarily delayed during the last few years, but the most extraordinary ingenuity was shown during the war in disposing of sewage and refuse matter under the most adverse conditions at many of the camps. It would seem that not only are our sanitary experts second to none in initiative, but that those who previously had had no experience in sanitation were able to adapt themselves in the most remarkable manner to meet the sanitary needs of all the complex situations arising out of the war. The imagination, initiative, and ingenuity displayed in sanitary matters during this period should in peace time bear rich fruit, and the writer believes that as a nation we shall again occupy a premier position in connection with all matters pertaining to public health.

Experiments in the purification of sewage by means of activated sludge continue to attract wide interest, and Mr. Haworth's highly ingenious notion of obtaining aeration by stirring instead of " air blowing " operations is the latest development in this line of investiga-

tion. At the moment of writing, Sheffield is putting down a unit capable of dealing with one million gallons a day, and the results will be eagerly awaited. Mr. Haworth (to whom the writer is much indebted for valuable information) prefers the word " bio-aeration " to " activated sludge " in describing this method of sewage treatment, and it certainly is a more scientific and apt description of what really takes place.

The following extract from Mr. Haworth's report to the Sewage Disposal Department of the City of Sheffield for the two years ended March 25, 1919, is full of interest:

" In a previous Report experiments have been described in which crude sewage was being treated by means of activated sludge. These experiments have been continued and developed, and two tanks on a working scale have been constructed recently, which are treating 50,000 to 60,000 gallons of trade sewage per day.

" Early in 1916 a tank of 800 gallons capacity was fitted with a paddle stirrer, and with an apparatus for inducing air mechanically. After this tank had been in use for some time it was found that by suitably regulating the revolutions of the paddle, purification could be obtained satisfactorily to the extent of at least three fillings of the tank per day, without the use of the aerator. The tank has been operated during the last two years in this manner. The following table indicates the character of the results obtained :

" *Analysis of Samples from Experimental Aeration Plant, Sheffield Sewage Works.*

From November 27, 1918, to January 31, 1919. Number of Samples, 45.   Results in parts per 100,000.

	Sewage			Effluent		
	Best	Worst	Aver	Best	Worst	Aver
Suspended solids . .	11·6	69·8	34·20	——	——	—
Oxygen absorbed in 4 hrs.	3·32	13·38	7·10	0·15	0·60	0·32
Free and saline ammonia	1·224	6·41	3·34	0·039	2·275	0·424
Albuminoid ammonia .	0·304	1·74	0·751	0·022	0·129	0·05
Chlorine	6·7	16·8	9·8	6·4	16·0	9·29
Nitric nitrogen . .	—	—	—	1·55	0·16	0·75
Dissolved oxygen taken in 5 days at 65° F. . .	—	—	—	0·013	0·389	0·153

" The results of this and other experiments led to the conclusion that given suitable agitation, to obtain thorough intermixing of the activated sludge with the sewage, and to prevent settlement, the necessary air required to maintain the biological activity might be obtained by surface aeration. To accomplish this it was found necessary to produce constant change of surface of the liquid.

" The question also suggested itself, and is worthy of investigation, whether in the case of systems where air is blown through the sewage,

the aeration is not largely brought about by solution at the surface, by reason of the large disturbance and change of surface exposed by the rising bubbles, rather than by solution of oxygen from the bubbles themselves. It was evident that, except in the case of small tanks, the horizontal paddle type of agitator would not be quite suitable, and two tanks of a different type have recently been designed and put into operation.

" The tanks are 30 ft. by 14 ft. by 4 ft. deep, with level floors. Division walls have been constructed to form a continuous channel, approximately 3 ft. 3 in. wide, along which the sewage can circulate and return to an agitator placed at one end of the tank. The agitator consists of two vertical pistons of the Root's blower type. On rotating the agitators, the sewage is circulated at a velocity sufficient to prevent settlement of the sludge. A velocity of $1\frac{1}{2}$ ft. to 2 ft. per second has been found ample to accomplish this result. The mechanical aerator was fixed in one of the tanks, in case additional air was required, but it has been found unnecessary. By means of the agitators and the special construction of the tanks constant change of surface occurs. One tank was put into regular use in October, 1918. Humus, washed from material taken from a contact bed, was put in to a depth of about 6 in. and the tank filled with sewage.

" After ten days' agitation the sludge was completely coagulated and flocculent, and found to be sufficiently activated to allow the experiment to proceed. The tank was then worked on the fill-and-draw principle, and has purified sewage satisfactorily and continuously during the last three months, three fillings of the tank per day being dealt with. The liquid treated is an industrial sewage, containing at times a large proportion of iron liquors, soaps, etc. These at times have required extended periods of treatment.

" The following table indicates the character of the sewage dealt with and the results obtained :

Analysis of Samples from Experimental Aeration Plant, Tinsley Sewage Works, Tank No. 1.

From November 29, 1918, to January 31, 1919. Number of Samples, 62. Results in parts per 100,000.

	Sewage.			Effluent.		
	Best	Worst.	Aver.	Best	Worst.	Aver.
Suspended solids . .	9·8	119·6	44·7	—	—	—
Oxygen absorbed in 4 hrs.	1·88	17·26	5·84	0·26	1·45*	0·76
Free and saline ammonia	1·208	5·632	2·525	0·110	3·024	1·249
Albuminoid ammonia .	0·364	3·560	1·131	0·062	0·277	0·13
Chlorine	4·1	14·7	8·5	5·8	12·1	8·6
Nitric nitrogen . . .	—	—	—	1·15	0·03	0·325
Dissolved oxygen taken in 5 days at 65° F. .	—	—	—	0·017	0·912	0·277

* Agitators stopped for two periods.

" The power absorbed by the process described is calculated at 20 horse-power per million gallons, but there appears. no doubt that the agitators employed could operate a much larger tank with only a slight additional power consumption. There is no doubt that a variety of types of agitator might be devised to operate such a process, probably with greater efficiency. Several types are at present under consideration. The Committee have already authorised the extension of the experiments to deal with the whole of the flow of their Tinsley works as soon as suitable plant can be obtained."

The great practical and scientific importance of W. D. Adeney's researches on the rate of solution of gases by water is attracting the attention of all those interested in the purification of water and sewage. His latest contribution (jointly with H. G. Becker) on the subject will be found in Vol. XV. (N.S.), No. 44 (Sept. 1919), of the *Scientific Proceedings of the Royal Dublin Society.* In their " Statement of Results " the authors say :

" From the figures given in the previous section it is possible to calculate the rate of solution of the gases dealt with, for any conditions of area exposed, depth or degree of saturation, provided that the water is kept uniformly mixed.

" The expression can be put either in the form

$$\frac{dw}{dt} = a - bw$$

which gives the rate of solution at any instant, or in the form $w = (w_0 - w_1)(1 - e^{-bt})$, which gives the amount dissolved at the end of any given time when $w_0 =$ saturation value and $w_1 =$ amount of gas in solution initially. For practical purposes it is most convenient to work in percentages of saturation ; hence the latter equation becomes $w = (100 - w_1)(1 - e^{-bt})$, and since

$$b = f\frac{A}{V}$$

by substitution

$$w = (100 - w_1)\left(1 - e^{-f\frac{A}{V}t}\right)$$

as the general equation for any given temperature, and since f varies with temperature according to the equations

Oxygen	$f = 0.0096$	$(T - 237)$
Nitrogen	$f = 0.0103$	$(T - 240)$
Air	$f = 0.0099$	$(T - 239)$

the corresponding general equation for each gas by substituting these expressions in the formulæ is obtained, thus :

For oxygen $\quad w \cdot (100 - w_1) \left[1 - e^{-0.0096(T-237)\frac{A}{V}t} \right]$

For nitrogen $\quad w \cdot (100 - w_1) \left[1 - e^{-0.0103(T-240)\frac{A}{V}t} \right]$

For air $\quad w \cdot (100 - w_1) \left[1 - e^{-0.0099(T-239)\frac{A}{V}t} \right]$

" As an example of the use of these formulæ, consider the question of the dissolved oxygen in 1000 c.c. of water, area exposed being 100 sq. cms., temperature 2·5° C., and initial gas content = 10% of saturation. How much gas will be dissolved in an hour ?

$t = 60$ minutes,

$w = 60(1 - e^{-0.0373t}) = 60(1 - e^{-0.222}) = 60(1 - 0.8009) = 60 \times 0.1991$

$= 11·8\%$ of saturation.

" Hence after an hour the water will have risen to 51·8% of saturation.

" These equations can also be used to calculate curves showing the rate of solution in water of the different gases under different conditions, and as an example the curves for oxygen between 0° C. and 30° C. have been calculated in percentages of saturation. It is noteworthy that when expressed in percentages of saturation the curves for the three gases lie very close to each other, those for oxygen and nitrogen being practically identical."

Some years have passed since the Royal Commission on Sewage Disposal [13] issued their final report, but it is really only now that the full force and significance of their recommendations are beginning to be adequately recognised, and the writer ventures to prophesy, on evidence much more valuable than his own experience, that the year 1919 marks the dawn of a growing appreciation of the great practical value of the Commission's labours.

The war, of course, has been partly responsible for this transitory period of relative stagnation of thought and action, but also it takes time to assimilate new ideas, especially when the questions dealt with cover a wide field of observation, are treated in an imaginative as well as a courageous and novel spirit, and embrace circumstances concerning which little was known, or if known, was open to controversial interpretation.

Much has been written about the Commission's work, but the writer agrees with those who think that the novel as well as the common-sense and logical basis of all their investigations and conclusions has been the keynote of their successful deliberations and is bound to attract

[13] Reference may be made to Mr. Kershaw's " *Guide to the Report of the Royal Commission on Sewage Disposal* " (Messrs. P. S. King & Son, Ltd.).

to a progressively increasing extent the favourable comment of all students of true progress.

After laboriously investigating the bacteriological qualities of all liquors and effluents from sewage purification processes, and coming to the conclusion that the methods of treatment failed to free these liquids from undesirable excremental bacteria, the Commissioners did not either advocate bacteriological standards, or suggest the necessity for sterilisation. On the contrary, they proceeded to take the bold line of judging effluents on a physical, chemical, and biological (exclusive of bacteria) basis. In doing so, they pointed out to waterworks authorities abstracting water for domestic use from polluted rivers the measure of their responsibilities and warned them that even if the danger from these liquids could be economically (a large assumption) removed, there would still remain the countless unavoidable contaminations which affect rivers flowing through, and draining, inhabited areas, which, in practice, can only be dealt with by purifying adequately the water after abstraction. In this connection it must always be remembered that even assuming the practicability of sterilising the dry-weather flow of sewage, it would be quite impracticable to deal with the whole volume of liquid which reaches a sewage works or escapes antecedently by overflows into rivers during periods of very wet weather.

As regards their suggested chemical standard (general standard for non-drinking water streams), this was based chiefly on two factors : (1) the desirability of preventing the accumulation of solid putrescible matter in the bed of rivers (not more than 3 parts of suspended matter in 100,000 parts of effluent is suggested), and (2) the importance of judging organic matter (in solution and in suspension) on the rational basis of its " decomposition value " (hence the standard of not more than 2 parts of dissolved oxygen used up in 5 days at $65°$ F. in the " whole " liquid, *i.e.*, including the sediment, is suggested). This is not a standard of the amount of organic matter in an effluent, but of that proportion of the total organic matter which alone really counts in its polluting effect on rivers. Without in the least criticising the value of other and perhaps simpler tests, the writer thinks the estimation of the amount of oxygen used up by an effluent is the truest criterion, scientifically and practically, of its behaviour when discharged into a stream. In framing their general and special standards the Commissioners took the opportune course of studying the quality of river waters and the effect as regards silting, growths, de-aeration, nuisance, etc., on river water of the discharge into them of effluents of variable quality and volume. Far from being satisfied with mere laboratory " findings " they subjected them to the crucial test of field observation. In this way they arrived at the important criterion figure of 0·4 part of dissolved oxygen taken up in 5 days as, generally speaking, the non-nuisance limit in the case of rivers. Rivers infringing this standard

were liable to become de-aerated, to show accumulations of black mal-
odorous mud and to encourage the development of unsightly grey
fungoid growths. On the other hand, rivers which did not exceed the
criterion figure were, on the whole, sweet, clean, and satisfactory in
the above respects. It should be noted that the general standard
(conveniently referred to as the 3/2 standard), which has been proved
to be attainable in practice, would not clash with this criterion figure
of 0·4, provided that the dilution of the effluent with river water was
at least 8 times and the river water *per se* did not absorb more than 0·2
part of dissolved oxygen in 5 days, both of which circumstances had
been shown by the Commissioners to be true in practice in the great
majority of instances. The foregoing by no means exhausts the fair
and common-sense (if the writer may say so with great respect) attitude
adopted by the Commission, for they recognised that no single figure,
no matter how carefully chosen, could possibly be suitable in exceptional
circumstances. They recognised that in a few cases the 3/2 standard
might not be sufficiently drastic, and in the others (the larger number)
quite unnecessarily severe in view of the local conditions. In the latter
cases they suggested special relaxed standards, based on the suspended
solids only, which may be designated as follows :

General Standard.—3/2. Not less than 8 dilutions.

Special Standards.—6/0 ; 150—300 dilutions. 15/0 ; 300.—500
dilutions. 0/0 ; over 500 dilutions.

The suggested machinery for giving effect to these recommendations
was a Central Authority controlling, co-operating with, and advising
Local Authorities.

Only one aspect of the Commission's work has been dealt with here,
but enough perhaps has been said to show that we shall at once be in a
position to make rapid progress in the purification of rivers without
imposing unnecessary hardships on sewage authorities, immediately
legislative effect is given to the recommendations of the Royal Com-
mission in regard to standards.

The writer calls attention in conclusion to the excellent Bibliographia
contained in the Supplemental Circular of the British Waterworks
Association. It aims at and succeeds in drawing attention to profes-
sional and technical papers and articles dealing with water supply and
cognate subjects. In the last Quarterly Circular (No. 26, Nov. 1919) of
the British Waterworks Association, the Secretary, Mr. Warner Terry,
gives under the heading " National Control of Water Sources " a most
valuable Digest of References to and Reports and Recommendations
of Royal Commissions, Special Committees of Parliament, Proceedings
of learned Societies and professional Institutions, and the opinions
of experts, on the subject of the National Control of Water Sources, the
establishment of Watershed Conservancy Authorities under a central
Government Authority, etc.

FINE CHEMICALS, MEDICINAL SUBSTANCES, AND ESSENTIAL OILS.

By T. A. Henry, D.Sc. (Lond.),

Director, Wellcome Chemical Research Laboratories.

This report has been compiled on much the same lines as those of previous years, but the arrangement of the sections has been altered, so that it now begins with naturally-occurring substances (alkaloids, glucosides, etc.) and concludes with synthetic products.

Alkaloids.

Quinine.

During the last thirty years Java has acquired a virtual monopoly in the production of cinchona bark, the only raw material available for the preparation of quinine and the related alkaloids, and as during the war the local manufacture of quinine was extended considerably the island is now in a strong position in the production of both bark and alkaloid.[1] In these circumstances it is only natural that proposals should be made for widening the area from which bark can be drawn. A. T. Gage[2] states that in peninsular India no effective addition can be made to the small areas already under cinchona, but suggests that planting on a large scale might be undertaken in the Tavoy district of Burma and that a Government quinine factory might be erected there. The district in question is rather remote and transport facilities are lacking, but as it has other natural resources of economic importance it is possible that the whole area may be rapidly developed. Attempts are being made to introduce cinchona cultivation in the Philippines,[3] and the manufacture of quinine in Brazil[4] and Colombia[5] has been proposed.

The preparation and properties of dihydroquinine homologues are still being investigated (*cf.* p. 499). M. Heidelberger and W. A.

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[1] *Bull. Imp. Inst.*, 1918. **16**, 370; *J.*, 1919, 60R, 420R.
[2] *Report on the Extension of Cinchona Cultivation in India*, 1919.
[3] *Ind. Engineering*, June 18, 1919.
[4] *U.S. Comm. Repts.*, Dec. 11, 1919; *J.*, 1919, 55R.
[5] *Midland Drugg. and Pharm. Rev.*, 1918, **52**, 310.

Jacobs [6] have prepared hydrocupreidine (the dextro-form of hydro-cupreine) and its ethyl ether, whilst E. Léger,[7] from a comparison of the action of sulphuric acid on hydroxyhydrocinchonine and the cinchonidine analogue, has assigned formulæ to both. P. Rabe and K. Kindler [8] have published the first of a series of papers on the synthesis of quinotoxines, in the course of which they describe a partial synthesis of dihydrocinchotoxine by condensing ethyl cinchoninate with ethyl N-benzoylhomocincholeupone,' in presence of sodium ethoxide, leading to the formation of the β-ketonic ester
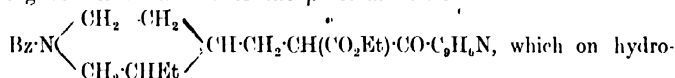
$$Bz\cdot N \underset{CH_2\cdot CHEt}{\overset{CH_2\quad CH_2}{\diagdown}} CH\cdot CH_2\cdot CH(CO_2Et)\cdot CO\cdot C_9H_6N,$$ which on hydro-

lysis yields dihydrocinchotoxine. As the latter has already been converted into cinchoninone, which in turn can be reduced by aluminium and sodium ethoxide to dihydrocinchonine and dihydrocinchonidine, this constitutes a partial synthesis of two naturally occurring cinchona alkaloids.

Morphine and the accompanying Alkaloids.

During the war Indian opium obtained for the first time in this country a definite footing as a raw material for the manufacture of morphine and codeine. Now that normal conditions are being restored it will be interesting to see whether this drug can hold its own in competition with Persian and " Turkey " opiums. It is clear from a report made recently by the Imperial Institute [9] that opium containing as much morphine and more codeine than Persian and " Turkey " opiums can be produced in India. It is understood that both the cultivation of the opium poppy and the preparation of opium are being investigated in India and that already considerable progress has been made.

A number of papers have been published during the year on the estimation of morphine, those by H. E. Annett and H. Singh [10] and by J. N. Rakshit and F. J. da Costa [11] being the outcome of experience with Indian opium.

Pelletierine and the associated Alkaloids.

K. Hess and collaborators,[12] continuing their work on the alkaloids of pomegranate root bark, have resolved pelletierine and methylisopelletierine into their optically active components. The pelletierines

[6] J. Amer. Chem. Soc., 1919, 41, 817 ; J., 1919, 734.
[7] Comptes rend., 1919, 168, 404 ; 169, 67.
[8] Ber., 1918, 51, 1360.   [9] Bull. Imp. Inst., 1919, 17, 1.
[10] Analyst, 1918, 43, 205 ; 1919, 44, 41 ; J., 1918, 441A, 1919, 197A ; cf. D. B. Dott, Pharm. J., 1918, 101, 318 ; J., 1919, 90A.
[11] Analyst, 1919, 44, 397 ; J., 1919, 876A.
[12] Ann. Repts., 1917, 2, 485 ; Ber., 1918, 51, 741 ; 1919, 52B, 964, 1005.

racemise to a considerable extent·on distillation, but this is not the case with the methyl*iso*pelletierines, due, it is suggested, to a difference in the side chain, which is —CH_2·CH_2·CHO in the former and —CO·CH_2·CH_3 in the latter. They also find that in the conversion of conhydrine into methyl*iso*pelletierine, some *dl*-methylconhydrinone is formed. Both these substances are α-1-methylpiperidylpropane-α-one and their isomerism is of a cis-trans type due to the presence of an asymmetric tervalent nitrogen and an asymmetric carbon atom. In the third paper it is shown that treatment of methyl*iso*pelletierine by cyanogen bromide [13] does not yield the expected *iso*pelletierine, but the demethylation can be successfully effected by means of ethyl azodicarboxylate.

The *iso*pelletierine so produced was subsequently found to be identical with an alkaloid prepared from the bark itself : this, like all the bases so far isolated by these authors from pomegranate root bark, is optically inactive.

Hyoscine and Hyoscyamine.

H. King [14] finds that *dl*-hyoscine can be resolved into its optically active components by crystallisation of the *d-α*-bromo-π-camphorsulphonate. In a second paper the same author confirms his previous suggestion that the two active hyoscines are partial racemates in which ·the optical activity is due to the tropyl radicle. A. McKenzie and J. K. Wood [15] have described an improved method of making tropic acid from acetophenone as a starting point : E. Muller's process [16] in their experience gives poor yields. The acid was resolved into its optically active components by the use of quinine for the *d*-form and morphine for the *l*-form ; the specific rotations found for the two forms are in close agreement with those recorded by King,[17] who resolved *dl*-tropic acid by the use of quinine and quinidine.

A. R. Cushny [18] has confirmed his previous conclusion that *l*-hyoscyamine is much more active than atropine, as indicated by its inhibiting action on the terminations of the *chorda tympani* stimulated by pilocarpine, and as the result of similar observations on other tropeïnes draws some general conclusions regarding the constitution and physiological action of the tropeïnes.

Anhalonium Alkaloids.

Mescal buttons, the flowering heads of various species of anhalonium used by Mexican Indians in religious ceremonies and as an intoxicant,

[13] *Ann. Repts.*, 1916, 1, 287.   [14] *Chem. Soc. Trans.*, 1919, 115, 476, 974.
[15] *Chem. Soc. Trans.*, 1919, 115, 828 ; *J.*, 1919, 654A.
[16] *Ann. Repts.*, 1918, 3, 443 ; U.S. Pat. 1305301 ; *J.*, 1919, 658A ; *cf.* W. Wislicenus and E. A. Bilhuber, *Ber.*, 1918, 51, 1237.   [17] *l.c. cit.*
[18] *J. Pharm. Exp. Ther.*, 1919, 13, 71 ; *cf.* H. A. D. Jowett, F. L. Pyman, and H. H. Dale, *7th Int. Cong. App. Chem.*, 1909, IVa, 1, 335, and F. L. Pyman, *Chem. Soc. Trans.*, 1917, 111, 1108.

have been repeatedly investigated since 1888. Seven alkaloids, all of comparatively low molecular weight, have been isolated, but to only one of these, mezcaline, has a constitution been assigned, and this was subsequently withdrawn by its author. This series of alkaloids has now been re-investigated by E. Späth,[19] who shows that they are all closely related. Anhaline is β-p-hydroxyphenylethyldimethylamine, $HO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot N(CH_3)_2$, and is therefore identical with hordenine. Mezcaline has been synthesised and shown to be β-3.4.5-trimethoxy-phenylethylamine. Anhalamine and pellotine are methyl ethers of 3.4.5-trihydroxyphenylethylamine whilst anhalonine and lophophorine each contain one methoxyl-group and two non-hydroxylic oxygen atoms.

Hydrastine and the related Bases.

K. W. Rosenmund [20] has described a new method of converting homo-piperonylamine into hydrastinine by the action of chloromethyl alcohol, and dehydration of the resulting homopiperonylaminomethanol, $CH_2O_2 \cdot C_6H_3 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2OH$, whereby Decker's dehydronorhy-drastinine is formed, which is then transformed into hydrastinine hydriodide by addition of methyl iodide. Homopiperonylamine not being readily obtainable, the same author describes the synthesis of two hydrastinine homologues by methods, identical in principle with that given above, starting from the more accessible substance, methylene-dioxyphenyl*iso*propylamine.

Harmine and Harmaline.

Harmine and harmaline, the alkaloids of *Peganum harmala* seeds, used as an anthelmintic in India and China, have been exhaustively studied by W. H. Perkin and R Robinson,[21] who suggest formula I as that most satisfactorily representing the reactions of harmine.

MeO   N   N $CH_2 \cdot CH_2(NH_2)CO_2H$

NH CH₃   NH CH₃   NH

I.   II.   III.
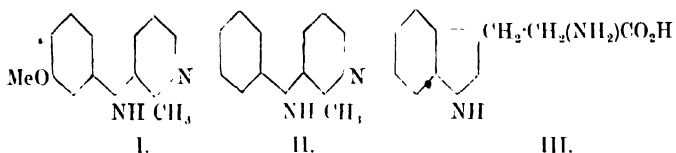
One of the most interesting observations made is that harman (II.), produced by the removal of the methoxyl group from harmine, is identical with a substance obtained by F. Gowland Hopkins [22] in 1902, by the oxidation of tryptophan (III.).

[19] *Monatsh. Chem.*, 1919, **40**, 129 ; *J.*, 1919, 843A.

[20] *Ber. deuts. pharm. Ges.*, 1919, **29**, 200 ; *J.*, 1919, 386A.

[21] *Chem. Soc. Trans.*, 1912, **101**, 1775 ; 1919, **115**, 933, 967 ; *J.*, 1912, 659 ; 1919, 791A.   [22] *J. Physiol.*, 1902, **29**, 451.

SIMPLE NATURAL BASES.

In the previous report [23] mention was made of E. C. Kendall's isolation of thyroxin (β-4.5.6-truodo-2-keto-4.5.6-trihydroindolepropionic acid) the hormone of thyroid gland. Since then the same author [24] has published a detailed description of the properties of the substance and the process of isolation. It is also stated that the substance was synthesised by Osterberg in 1917, and that this work was repeated and confirmed in 1919, but no account of the synthesis has yet been published.

Thyroxin, in addition to pilocarpine and tethelin, has been tried in certain acute cases of avian polyneuritis and found to afford relief, though the response was not of the same type as that produced by preparations containing vitamines.[25] This observation is to some extent complementary to that of F. Uhlmann,[26] who found that on various tissues preparations containing vitamines exerted much the same action as pilocarpine and choline, such action being likewise antagonised by atropine.

G. Barger and F. Tutin [27] have shown that 2·4.5-trinitrotoluene condenses with amino-acids, the latter becoming attached to the benzene ring by the amino group in replacement of a nitro-group. The reaction does not take place with imino-groups, but occurs with the free amino-groups of peptides and thus affords a means of ascertaining the constitution of these substances, since on hydrolysis of their condensation products with trinitrotoluene only those amino-acid radicles which originally had free amino-groups, will remain attached to the benzene ring. In the case of carnosine the condensation product on hydrolysis yields dinitrotolyl-β-alanine ; thus supporting the view first put forward by W. von Gulewitsch [28] that carnosine is β-alanylhistidine and subsequently proved to be correct by L. Baumann and T. Ingvaldsen's [29] synthesis of the base by condensing β-iodopropionyl chloride with histidine.

In confirmation of the view expressed previously,[30] J. J. Abel and S. Kubota [31] state that the oxytoxic principle of the hypophysis is not specific to that organ, but is a substance widely distributed in animal tissues and is probably histamine (β-iminazolylethylamine). The latter was isolated from the pituitary tissue and the gastric and intestinal mucosa of the dog and was detected in liver tissue and in striated muscle.

[23] *Ann. Repts.*, 1918, **3**, 451.
[24] *J. Biol. Chem.*, 1919, **39**, 125; with Osterberg, *ibid.*, 1919, **40**, 265.
[25] R. A. Dutcher, *J. Biol. Chem.*, 1919, **39**, 63.
[26] *Zeits. Biol.*, 1918, **68**, 419, 457 ; *J.*, 1918, 715A.
[27] *Biochem. J.*, 1918, **12**, 402 ; *J.*, 1919, 196A.
[28] *Z. physiol. Chem.*, 1911, **73**, 434.   [29] *J. Biol. Chem.*, 1918, **35**, 263.
[30] *Cf. Ann. Repts.*, 1917, **2**, 492.   [31] *J. Pharm. Exp. Ther.*, 1919, **13**, 243.

K. K. Koessler and M. T. Hanke [32] have published an account of the production of histamine from histidine by *Bacillus coli communis*, in which they state that in presence of oxygen and in a medium containing histidine, glycerol or glucose, and a suitable source of nitrogen, such as potassium nitrate or ammonium chloride, about 50% of histidine is converted into histamine. The quantitative work on which this paper is based has been made possible by the use, under specified conditions, of the diazo reaction as a means of estimating either histamine or histidine colorimetrically,[33] a quantitative separation of the two bases being effected by extraction of the histamine with amyl alcohol [34] from a solution containing 20% of sodium hydroxide. From a preliminary announcement it appears that work on similar but more comprehensive lines is also being carried out in this country under the auspices of the Medical Research Committee.[35]

In the course of an attempt to realise Gowland Hopkins' suggestion that purine derivatives may originate from histidine in the animal body, F. L. Pyman and R. G. Fargher [36] have investigated the possibilities of preparing amino-substituted glyoxalines by reduction of the corresponding nitro- and arylazo-derivatives. The latter, which form the basis of a colour reaction almost universally used for the detection of glyoxaline derivatives in biological chemistry (see above), are shown to be C-azo and not N-azo compounds as has hitherto been supposed.

H. D. Dakin [37] has devised a method of separating amino-acids produced in the hydrolysis of proteins, which depends on the continuous extraction of a neutralised, concentrated solution resulting from such hydrolysis, with hot butyl alcohol. The latter removes (1) aliphatic and aromatic monoamino acids, which deposit as the extraction proceeds, (2) proline, and (3) peptide anhydrides (diketopiperazines) which remain dissolved in the butyl alcohol. Two other groups remain in the aqueous solution, viz. dicarboxylic acids and diamino-acids, and can be separated by precipitation of the latter with phosphotungstic acid or other means. The method has been applied to caseinogen, and it is pointed out that in this case the mixture of amino-acids (Group 1 above) which includes leucines, alanine, valine, phenylalanine, and a little tyrosine, is obtained as a cream-coloured, granular powder, which is suitable as a base for nutrient media, with or without addition of tryptophan, and that as it is free from most of the amino-acids which yield glucose in the diabetic organism it may have dietetic possibilities.

[32] *J. Biol. Chem.*, 1919, **39**, 539.
[33] *Ibid.*, 497.   [34] *Ibid.*, 521.
[35] *Fifth Annual Report of the Medical Research Committee*, 1919, p. 66.
[36] *Chem. Soc. Trans.*, 1919, **115**, 217, 1015.
[37] *Biochem. J.*, 1918, **12**, 290; *J.*, 1919, **106A**.

GLÜCOSIDES.

Activity in the investigation of digitalis and its protean constituents shows no signs of diminishing but the position remains the same as already reported.[38]

This year's papers deal principally with the stability of digitalis and its preparations under various conditions,[39] or with methods for the extraction of the whole of the active principles, or for the evaluation of the drug [40] by chemical or physiological methods.   Two papers by H. Kiliani,[41] dealing with secondary digitalis constituents, form the most important contributions to the chemistry of the drug.

Experiments in the breeding of different races of foxgloves at Cambridge have shown that the digitalin content is correlated with the external characters of smoothness or hairiness of the leaf.[42]   According to G. P. Koch and J. R. Butler [43] the activity of digitalis is increased by about 17% when manganese sulphate is applied as a dressing to the soil in which the drug is grown.

W. Straub [44] states that oleander leaves are $2\frac{1}{2}$ times as active as digitalis leaves and contain constituents which can be extracted by cold water and are similar in character to certain of those present in digitalis.

The well-known drug squills, which has lately come into prominence as a rat poison, has been subjected to a preliminary investigation by E. Buschmann.[45]

The saponins form an interesting group of glucosides about which very little is known beyond the facts that their solutions in water froth on agitation and possess detergent properties.   Some of them, such as digitonin, form crystalline compounds with certain alcohols and many of them possess hæmolytic properties.   They find industrial application for producing foam in certain types of fire-extinguishers and are sometimes used in the textile industry as detergents.   Occasionally they are employed for suspending oily liquids in water, and the use of such materials as Chinese tea-seed cake for destroying worms on lawns depends on the presence of saponin.   Certain drugs, such as senega, are also believed to owe such activity as they possess to saponins or

[38] Ann. Repts., 1916, 1, 290 ; 1918, 3, 445.

[39] J. M. Schmidt and F. W. Heyl, Amer. J. Pharm., 1919, 91, 425 ; J., 1919, 654A.   H. C. Hamilton, J. Amer. Chem. Soc., 1919, 41, 125 ; J., 1919, 198A.

[40] A. Tschirch and F. Wolter, Schweiz. Apoth. Zeit., 1918, 56, 469 ; J., 1919, 386A.   E. Berry, Phar. J., 1919, 103, 69 ; J., 1919, 654A.   C. Mannich, Ber. deuts. pharm. Ges., 1919, 29, 206 ; J., 1919, 387A.   G. Joachimoglu, ibid., p. 170.

[41] H. Kiliani, Ber., 1918, 51, 1613 ; 1919, 52, 200 ; J., 1919, 54A, 477A.

[42] 4th Report Medical Research Committee, Cd. 8981, 1918, p. 72 ; 5th Annual Report M.R.C., Cd. 412, 1919, p. 67.

[43] Amer. J. Pharm., 1919, 91, 211 ; J., 1919, 438A.

[44] Arch. Exp. Pathol. u. Pharmacol., 1918, 82, 327 ; J., 1919, 27A.

[45] Arch. Pharm., 1919, 257, 79.

similar substances. In view of their growing importance it is interesting to note that E. Winterstein and M. Maxim [46] have begun the investigation of saponin-yielding materials with a study of soap-berries (*Sapindus saponaria*). These berries appear to contain a mixture of complex glucosides, which can be gradually hydrolysed into a mixture of sugars (hexoses 45%, pentoses 15%) and sapogenins (33–35%). On bromination the foaming power remains unimpaired, but the hæmolytic activity is lost and the bromo-derivative inhibits the hæmolytic action of other saponins.

Alfalfa saponin, according to C. A. Jacobsen, [47] yields pentose, dextrose, and a sapogenin on hydrolysis and differs from most saponins by containing nitrogen and in exhibiting no hæmolytic activity. It is not toxic when taken *per os* though it causes severe local irritation and death when injected subcutaneously. Its aqueous solution has a remarkably high surface tension. The saponin of *Platycodon grandiflorum*, isolated by H. Oshika, [48] is hæmolytic and toxic. According to A. L. Flohr [49] pancreatic lipase is activated by saponin, the influence exerted increasing with the concentration of the saponin up to 2% and then diminishing. It exerts a reverse action with castor seed lipase and in this case the effect increases steadily with the concentration of the saponin.

ESSENTIAL OILS.

Among the publications of general interest on this subject which have appeared during the year reference may be made to the address on the botanical distribution and characters of some odorous principles of plants delivered to the Washington Chemical Society by F. B. Power, [50] and to the paper by T. H. Durrans, [51] in which an attempt is made to trace the relationship between chemical constitution and odour in compounds containing the three elements carbon, hydrogen, and oxygen. In this connection the author calls attention to the frequency with which • unsatisfied partial valencies or residual affinities, such as those due to the tetravalency of oxygen, occur in odorous substances and suggests that this may be the primary cause of the odour.

Considerable activity has been shown in devising methods for the utilisation of *p*-cymene, the chief constituent of " spruce turpentine," now obtainable in considerable quantities as a by-product of the pulp industry. Cymene is readily convertible into carvacrol by nitration, reduction, and diazotisation, or through the monosulphonic acid, and .

[46] *Helv. Chim. Acta*, 1919, **2**, 195; *J.*, 1919, 303A.

[47] *J. Amer. Chem. Soc.*, 1919, **41**, 640; *J.*, 1919, 176A.

[48] *Jap. Med. Literature*, 1919, **4**, 20.

[49] *Arch. Neerland. Physiol.*, 1919, **3**, 182.

[50] *J. Ind. Eng. Chem.*, 1919, **11**, 344; *J.*, 1919, 337A.

[51] *Perf. Essent. Oil Rec.*, 1919, **10**, 104; *J.*, 1919, 479A.

both methods are the subject of recent patents and papers.[52] Carvacrol is, however, in no great demand commercially and the work has been extended to find derivatives of industrial value. The most promising of these appears to be amino-carvacrol ($OH:Me.NH_2:Pr\beta$ 1:2:1:5) which can be used as a photographic developer and is readily prepared from the nitroso-derivative, obtainable in almost quantitative yield by the action of sodium nitrite on the phenol. Whilst it seems likely that the supply of carvacrol will soon be in excess of the demand the reverse is the case with thymol, the demand for which is rapidly increasing owing to its use as an anthelmintic in the campaigns against ankylostomiasis now in progress in various tropical countries. It seemed likely that the introduction of chenopodium oil for this purpose would relieve the situation, but so far is this from being the case that chenopodium oil has also risen greatly in price and towards the end of the year supplies were difficult to obtain, though attempts are being made to produce the oil in new areas such as India and Java. In these circumstances it seems desirable that recourse should be had to other remedies such as β-naphthol, eucalyptus with chloroform, quassiin, male fern oil, etc., all of which have their advocates among experts on tropical diseases. It is possible, however, that cymene may also become available as a source of thymol since C. E. Andrews[53] has patented a method of making it by nitrating aminocymene, the amino-group, protected during the nitration, being subsequently eliminated ;   he nitrocymene so obtained is then converted into thymol through the diazo-compound.

A new source of thymol has been recorded from Japan, the oil from *Mosla japonica*[54] yielding 50% of thymol : that from *M. grosserrata*[55] yields carvacrol.

Another interesting Japanese oil is that from the leaves of *Perilla citriodora*,[56] which contains over 59% of citral   The allied plant *P. arguta*[57] yields, according to Gattefosse, 55% of aldehydes, chiefly • dihydrocuminic aldehyde, with an alcohol which may be identical with that of ginger-grass oil. A Japanese plant yielding an oil rich in geraniol (63·5%) is *Pelargonium denticulatum*[58] : *P. graveolens* and *P. radula*,

[52] A. W. Hickson and R. H. McKee, U.S. Pat. 1265800; *J.*, 1918, 531A ; *J. Ind. Eng. Chem.*, 1918, **10**, 982 ; *J.*, 1919, 55A. C. E. Andrews, *ibid.*, 1918, **10**, 153 ; *J.*, 1918, 486A. U.S. Pat. 1314920; *J.*, 1919, 813A. O. Aschan, *Chem. Zentr.*, 1919, I , 227. H. A. Lubs, *J. Ind. Eng. Chem.*, 1919, **11**, 455 ; *J.*, 1919, 478A, 795A. J. A. Ambler and H. A. Lubs, U.S. Pat. 1316823 ; *J.*, 1919, 813A.
[54] U.S. Pat. 1306512 ; *J.*, 1919, 658A.
[54] K. Hoshino, *J. Chem. Ind. Tokyo*, 1919, **22**, 357 ; *J.*, 1919, 877A.
[55] S. Furukawa, *ibid.*, 1919, **22**, 382 ; *J.*, 1919, 877A.
[56] H. Kondo and S. Yamaguchi, *J. Pharm. Soc. Japan*, 1919, **446**, 263.
[57] *Perf. Essent. Oil Rec.*, 1919, **10**, 170 ; *J.*, 1919, 553A.
[58] S. Furukawa, *J. Chem. Ind. Tokyo*, 1919, **22**, 83 ; *J.*, 1919, 656A.

also examined, yield oils of less value.   A number of papers [59] on new or little known sources of turpentine oil have also been published, those by O. Aschan including a résumé of the chemistry of the terpenes.

There seems to have been less activity than usual in the investigation of the constitution and reactions of the components of essential oils. Among the more important papers of this type are those on ketones of the ionone and irone type by L. Ruzicka,[60] who has also accomplished, with V. Fornasir, a new synthesis of linalool, which confirms Tiemann and Semmler's formula for this alcohol.   Knoevenagel [61] and his collaborators have published a long paper on the condensation of citral with acetoacetic ester.

P. Sabatier, A. Mailhe, and G. Gaudion [62] find that pinene passed over finely divided copper at 550° C. gives a 21% yield of aromatic hydrocarbons, including toluene, m-xylene, cymene, cumene, and methylethylbenzene.

SYNTHETIC DRUGS.

During the year a number of papers have appeared dealing with the manufacture of synthetic drugs and the organisation of research on this subject in this country [63] and in France,[61] the United States,[65] and Japan.[66]

Hypnotics.

In a previous report [67] it was mentioned that hydantoin may be utilised as the nucleus of substances possessing hypnotic properties, " nirvanol " (phenylethylhydantoin) being a product of this type.   This substance and its analogues can be prepared by the action of hypochlorite or hypobromite solutions on (1) CC-arylalkylcyanoacetamide or (2) disubstituted malonamides.   Thus " nirvanol " (I) can be made either from phenylethylcyanoacetamide (II) or phenylethylmalonamide (III).

$$
\text{(I)} \begin{array}{c} \text{Ph} \\ \\ \text{Et} \end{array} \!\!>\!\! \text{C} \!\!<\!\! \begin{array}{c} \text{NH·CO} \\ | \\ \text{CO·NH} \end{array} \quad
\text{(II)} \begin{array}{c} \text{Ph} \\ \\ \text{Et} \end{array} \!\!>\!\! \text{C} \!\!<\!\! \begin{array}{c} \text{CO·NH}_2 \\ \\ \text{CN} \end{array} \quad
\text{(III)} \begin{array}{c} \text{Ph} \\ \\ \text{Et} \end{array} \!\!>\!\! \text{C} \!\!<\!\! \begin{array}{c} \text{CO·NH}_2 \\ \\ \text{CO·NH}_2 \end{array}
$$
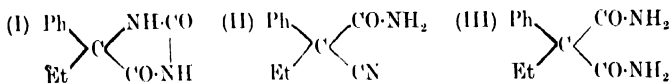
In a third patent the method is generalised and it is claimed that alkylarylhydantoins may be made by condensing substances

[59] Y. Shinosaki, *ibid.*, 1918, **21**, 763 ; ,1919, **22**, 451 ; *J.*, 1919, 21A, 877A.
O. Aschan, *Chem. Zentr .*, 1919, **90**, 1 , 284, 285 ; *J.*, 1919, 656A.
[60] *Helv. Chim. Acta*, 1919, **2**, 144, 182, 352 ; *J.*, 1919, 303A.
[61] *J. prakt. Chem.*, 1918, ii, 97, 288.
[62] *Comptes rend.*, 1919, **168**, 926 ; *J.*, 1919, 439A.
[63] F. H. Carr, *J.*, 1919, 259T ; National Health Insurance Commission, *Cmd.* 183 ; '*J.*, 1919, 292R.
[64] A. Detoeuf, *Chim. et Ind.*, Feb., 1919 ; *J.*, 1919, 136R.
[65] *J. Ind. Eng. Chem.*, 1919, **11**, 59, 157, 377.
[66] *J.*, 1919, 269R.   [67] *Ann. Repts.*, 1917, **2**, 479.

of the following three types: $RR'\cdot C(NH\cdot CO\cdot NH_2)COOH$; $RR'\cdot C(NH\cdot COOH)CO\cdot NH_2$; $RR'\cdot C(NH_2)CO\cdot NH\cdot COOH$.[68]

The combination of disubstituted barbituric acids with dialkylamines such as dimethylamine or diethylamine is stated to produce readily soluble compounds with enhanced hypnotic properties.[69]

Local Anæsthetics.

There is little new work to record on local anæsthetics. A. E. Everest[70] finds that in the preparation of diacetonamine, an intermediate required in the manufacture of "*p*-eucaine," absorption of ammonia by acetone is facilitated by the presence of dry calcium chloride, the yield being improved and the duration of the operation much shortened.

In a recent patent[71] the preparation of β-bromoethyl p-nitro-benzoate, $CH_2Br\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, is claimed with a view to its use in the manufacture of "novocaine." It is made by heating a p-nitro-benzoate with excess of ethylene dibromide in presence of an amine, or finely divided copper, as a catalyst. The bromo-ester is then treated with diethylamine, and by subsequent reduction of the nitro-group "novocaine" $CH_2(NEt_2)\cdot CH_2\cdot O\cdot CO\cdot C_6H_4NH_2\cdot HCl$ is obtained.

A. Ogata[72] has prepared a series of α- and β aminoalkyl (aryl) ben-zenes with a view to studying the relationship between their constitution and physiological action. The hydrochlorides of β-amino-α-phenyl-octane $\alpha\beta$-diphenylethylamine, α-phenylethylamine, benzyl-β-phenyl-*iso*propylamine and *iso*amyl*iso*hexylamine showed a local anæsthetic action when applied to the tongue.

J. Morgenroth[73] has published a study of the influence of stereoiso-merism on anæsthetic action based on the examination of hydro-cupreine derivatives and their isomerides. Of the two stereoisomerides *iso*amylhydrocupreine ("eucupine") and *iso*amyl*apo*hydroquinidine, the former is twice as potent an anæsthetic as the latter. As the struc-tural isomeride, eucupinotoxine, is also an anæsthetic it appears that this property is not dependent on the presence of the quinuclidine nucleus, since a great increase in the potency takes place with the rupture of the carbon-nitrogen linkage, eucupinotoxine being far more active than eucupine and forty to fifty times as powerful as cocaine. The author concludes that the trypanocidal, bactericidal, and anæsthetic

[68] Chem. Fabr. von Heyden, A.-G., Ger. Pats. 309508, 310426, 310427; *J.*, 1919, 389A, 440A.

[69] F. Hoffmann-La Roche & Co., Eng. Pat. 122778, U.S. Pat. 1316047; *J.*, 1919, 233A, 848A.

[70] *Chem. Soc. Trans.*, 1919, **115**, 588; *J.*, 1919, 655A.

[71] The Abbott Laboratories, U.S.A., Eng. Pat. 121578; *J.*, 1919, 268A.

[72] *J. Pharm. Soc. Japan*, 1919, **445**, 193.

[73] *Ber. deuts. pharm. Ges.*, 1919, **29**, 233; *J. Chem. Soc.*, 1919, **116**, i., 300.

action are common to the quinotoxines and the original alkaloids, the difference in activity of ethylhydrocupreine and ethylhydrocupreinotoxine towards pneumococci being exceptional. Anæsthetic action is influenced but not conditioned by space arrangement; the one instance quoted to the contrary, viz., the supposed difference in the action of benzoyltropeine and benzoyl-ψ-tropeine,[74] is shown to be inaccurate.

Antipyretics.

M. T. Bogert and J. Ehrlich [75] have described the preparation of 3·5-dimethoxy-4-ethoxyacetanilide from the ethyl ether of syringic acid. The latter is converted into the chloride and amide and thence by the Hofmann reaction to 3,5-dimethoxy-4-ethoxyaniline which on acetylation yields the corresponding acetanilide; this compound exhibits marked antipyretic properties and is not more toxic than phenacetin.

J. Tcherniac [76] has protected the preparation of hydroxyalkyl ethers of p-hydroxyacetanilide, by the use of monohalogen-hydrins. According to L. Thorp [77] p-ethoxy-α-bromodiethylacetanilide, prepared by the action of an acyl halide of α-bromodiethylacetic acid on p-ethoxyaniline, possesses analgesic and sedative properties, which are also common to its analogues derived from other arylamines.

2.2'-Thienylquinoline-4-carboxylic acid, $C_4H_8S \cdot C_9H_5N \cdot COOH$, prepared by M. Hartmann and E. Wybert,[78] resembles and exceeds 2-phenylquinoline-4-carboxylic acid (" atophan ") in analgesic properties, but on administration by the mouth or intravenously produces in the animal a violet-red colour, which is persistent and appears in almost all the internal organs.

Organic Compounds of Arsenic.

In the United States a number of papers [79] have been published dealing with the preparation of well-known arsenic compounds. Among these is a paper by W. A. Jacobs and M. Heidelberger,[80] who show that in the action of arsenic acid on phenol some o-hydroxyphenylarsinic acid is formed, in addition to the para-acid, and may be isolated as a basic barium salt, after the removal of the para-acid as the sodium salt. There are also produced in small quantities pp'-dihydroxydiphenylarsinic acid, and a substance which is believed to be the op'-isomeride. In the analogous reaction of arsenic acid with aniline F. L.

[74] Cf. S. Fränkel, " Die Arzneimittel Synthese," Berlin, 1912, p. 359.
[75] J. Amer. Chem. Soc., 1919, 41, 798.
[76] Eng. Pat. 120081; J., 1919, 27A.
[77] U.S. Pat. 1279042; J., 1919, 28A.   [78] Helv. Chim. Acta, 1919, 2, 60.
[79] P. A. Kober and W. S. Davis, J. Amer. Chem. Soc., 1919, 41, 451; P. A. Kober, ibid., 442; J. B. Conant, ibid.. 431.
[80] J. Amer. Chem. Soc., 1919, 41, 1440; J., 1919, 922A.

Pyman and W. C. Reynolds [81] had already shown that small quantities of pp'-diaminodiphenylarsinic acid are produced. R. G. Fargher [82] has now prepared from this acid by diazotisation and subsequent nitration 3.3'-dinitro-4.4'-dihydroxydiphenylarsinic acid. On suitable treatment with sodium hyposulphite this acid yielded the corresponding diamino-acid and 3.3'-diamino-4.4'-dihydroxydiphenylarsenious hydroxide. The former on further reduction with hypophosphorous acids gave 3.3'.3''.3'''-tetramino-4.4'.4''.4'''-tetrahydroxytetraphenyldiarsine $(NH_2 \cdot C_6H_4 \cdot OH)_2 \colon As \cdot As \colon (HO \cdot C_6H_4 \cdot NH_2)$.

Various metallic derivatives of " salvarsan " are under clinical trial and promising results have been obtained with " silver salvarsan " in a series of 54 cases at Frankfurt, including various types of syphilis, tabes, etc. [83]

G. Giemsa [84] has published some observations on hexamino-arseno-benzene, which has been known since 1913, and which yields a readily soluble sulphamic acid, $(NH_2)_3(C_6H_2 \cdot As \colon As \cdot C_6H_2(NH_2)_2 \cdot NHSO_3H$, and a diethyl derivative, $NHEt(NH_2)_2C_6H_2 \cdot As \colon As \cdot C_6H_2(NH_2)_2 \cdot NHEt$ (" ethyl-arsalyte "). These products are stated to be not only therapeutically valuable, but to yield solutions which can be kept for long periods, when suitable precautions, apparently realisable in practice, are taken.

R. R. Baxter and R. G. Fargher [85] have described recently the preparation of 1.3-benzodiazole-5-arsinic acid, $CH \underset{N}{\overset{NH}{\lessgtr}} C_6H_3 \cdot AsO_3H_2$, and a number of its homologues, and the conversion of these into the corresponding arsenobenzenes.

In the United States the Rockefeller Institute [86] has been giving attention to the preparation of derivatives of N-phenylglycine-p-arsinic acids in which the aromatic nucleus containing the arsenic radicle is attached to the a-amino group of an a-aminoacylamino side-chain. There thus result substituted arsinic acids from which, by controlled reduction, the corresponding arsenoxides and arsenobenzenes are produced. The initial products are prepared by treating sodium p-aminophenylarsinic acid with amides, ureides, or anilides of halogenated acetic acids or by the action of an amine on the methyl ester of N-phenylglycine-p-arsinic acid. Variation thus depends on the nature of the side-chains, and the compounds so far prepared have side-chains of the following three types. (I) $\cdot NH \cdot CHR \cdot CO \cdot NR'_2$, (II) $\cdot NH \cdot CHR \cdot CO \cdot NH \cdot$

[81] *Chem. Soc. Trans.*, 1908, **93**, 1184.   Cf. L. Benda, *Ber.*, 1908, **41**, 2371.
[82] *Chem. Soc. Trans.*, 1919, **115**, 982; *J.*, 1919, 843A.
[83] Dreyfus, *Med. Klinik*, 1919, **15**, 806.
[84] *Deuts. Med. Woch.*, 1919, **45**, 94; *J.*, 1919, 598A.
[85] *Chem. Soc. Trans.*, 1919, **115**, 1372.
[86] W. A. Jacobs, W. H. Brown, M. Heidelberger, and L. Pearce, U.S. Pats. 1280119–1280127; *J.*, 1919, 268A.

CO·NRH, (III) ·NH·CHR·CO·NHR″, where R may be hydrogen, alkyl, or aryl, R′ hydrogen or alkyl, and R″ is an aryl radicle, with or without nuclear substituents. These compounds, which are stated to be potent trypanocidal and spirochæticidal agents, are dealt with in the first three patents. The next two relate to the reduction products and deal with (A) the arsenoxides, containing the group -AsO corresponding to amides and anilides (side-chains I and III above) already referred to, and (B) the arsenophenylglycine*bis*arylamides produced by more vigorous reduction, with hypophosphorous or hydriodic acid, of the anilides (side-chain III) resulting in the combination of two molecules of the reduced substituted anilide through the group -As:As-. This last series of compounds is stated to be of greater therapeutical value than any of the initial substances. The last four patents deal with the production of soluble salts, the first three relating to sodium salts of the initial amides, ureides, and anilides and the last to salts, for example with hydrochloric acid, of the arsenoaryl condensation products.

A number of other patents [87] relating to arsenical compounds have been taken out in the United States of which that by W. Grüttefien describes salts of the alkaloid yohimbine with arsenic, methylarsinic, phenylarsinic, and other acids. These are stated to be useful therapeutic agents, which unlike their components are devoid of any irritant effect in the intestines.

COMMERCIAL SYNTHESES OF THE SIMPLER ALIPHATIC COMPOUNDS.

Halogenated Compounds.

The chlorination of open-chain hydrocarbons was reviewed somewhat fully in the two previous reports,[88] and as the work published since then deals mainly with details of methods it can be disposed of briefly The United States Bureau of Mines has issued a report stating that natural gas can be chlorinated in one operation by the use of catalysts having high adsorption values for chlorine, to yield chloroform, carbon tetrachloride, and hexachloroethane.[89] Further details are given in a paper by G. W. Jones and V. C. Allison,[90] from which it appears that suitable catalysts are " war-gas charcoal," steamed anthracite, and " bachite " (a specially prepared carbon) : other forms of carbon, alone or impregnated with metals or metallic oxides, allow part of the chlorine to pass. Reaction begins at 250° C. and increases in intensity up to 500° C., after which carbon begins to be deposited. The proportions of the three products obtained depend largely on the relative proportions of the components of the gaseous mixture used.

[87] K. J. Oechslin, U.S. Pats. 1299214 and 1299215 ; cf. J., 1916, 275 ; J. M. White, U.S. Pats. 1313657 and 1297952 ; J., 1919, 795A, 847A ; M. Grüttefien, U.S. Pat. 1305462 ; M. Guggenheim and E. Hug, U.S. Pats. 1308413 and 1308414 ; J., 1919, 659A.   [88] *Ann. Repts.*, 1917, **2**, 468 ; 1918, **3**, 430.
[89] *J.*, 1919, 329R.   [90] *J. Ind. Eng. Chem.*, 1919, **11**, 639 ; J., 1919, 599A.

H. T. Boyd [91] chlorinates the lower paraffins above methane by the use of liquid chlorine, the vapours from the reaction being then treated with gaseous chlorine in a separate chamber. Liquid chlorine is also employed by G. O. Curme [92] to convert ethylene into the dichloride, the hydrocarbon being used in either gaseous or liquid form. The ethylene can be purified through the mercury compound formed when the gas is passed into a solution of a mercury salt. Propylene under similar conditions yields the dichloride.

According to V. J. Harding, [93] brick, pumice, sand, coke, charcoal, ferric oxide, alumina, and magnesia, heated to 50°–150° C., act as catalysts in the chlorination of olefines to dichloroparaffins.

Tetrachloroethane, prepared by passing a mixture of chlorine and acetylene over heated iron filings and quartz, yields trichloroethylene on treatment with ammonia and water.[94] V. R. Kokatnur [95] has examined the influence of catalysts on the chlorination of hydrocarbons by passing chlorine into acetylene tetrachloride containing vegetable charcoal, animal charcoal, or metallic iron   Hexachloroethane is the only product formed, though when chlorination is attempted with aluminium chloride or bleaching powder the tetrachloride is partially converted into *unsym*tetrachloroethane.

J. Feyer [96] has published a study of the electrolytic preparation of chloroform under various conditions, especially in solutions of alkali and alkaline-earth chlorides. H. H. Dow [97] has protected a process for preparing chloroform by the reduction of carbon tetrachloride. The latter has also been used as a source of carbonyl chloride by heating it with sulphuric anhydride or pyrosulphuric acid,[98] or, according to C. Maugum and L. J. Simon,[99] ordinary sulphuric acid.   H. B. Weiser and G. E. Wightman [100] state that carbon tetrachloride is decomposed into chlorine and tetrachloroethylene at temperatures as low as 600° C., but the best yield of the latter is obtained at 1300°–1400° C.   The products require to be cooled rapidly to minimise the formation of hexachloroethane.

R. Adams and V. Voorhees [101] have modified Walker's method for the preparation of alkyl iodides to make it suitable for the production of

[91] U.S. Pat. 1293012 ; *J.*, 1919, 304A.
[92] U.S. Pats. 1315545, 1315541, 1315547 ; *J.*, 1919, 547A, 548A.
[93] Eng. Pat. 126511 ; *J.*, 1919, 513A.
[94] Comp. des Prod. Chim. d'Alais et de la Camargue, Eng. Pats. 132755 and 132757 ; *J.*, 1919, 547A.
[95] *J. Amer. Chem. Soc.*, 1919, **41**, 120 ; *J.*, 1919, 199A.
[96] *Z. Electrochem.*, 1919, **25**, 115 ; *J.*, 1919, 599A.
[97] U.S. Pat. 1311329 ; *J.*, 1919, 740A.
[98] V. Grignard and E. Urbain, *Comptes rend.*, 1919, **169**, 17 ; *J.*, 1919, 574A.
[99] *Ibid.*, p. 34 ; *J.*, 1919, 575A.
[100] *J. Phys. Chem.*, 1919, **23**, 415 ; *J.*, 1919, 655A.
[101] *J. Amer. Chem. Soc.*, 1919, 41, 789 ; *J.*, 1919, 478A.

considerable quantities of methyl, ethyl, propyl, *n*-butyl, and *iso*amyl iodides.

A number of patents have been taken out dealing with plant or details of processes for the manufacture of chlorohydrins by the interaction of chlorine and water (liquid or vapour) with olefines from various sources, including natural gas.[102] Others, having the same object in view, utilise the action of hypochlorous acid on olefines, the variations being chiefly in the mode of producing or applying the acid,[103] whilst in one case the change is effected by the action of a reducible chloride on the appropriate olefine.[104]

Alcohols.

Much of the work on alcohols published during the year relates to their production by fermentation, butyl alcohol and glycerol being the chief subjects of these communications. R. Adams, O. Kamm, and C. S. Marvel [105] state that *tert.* amyl alcohol can be prepared in a yield of 80 to 90% by the addition of amylene to sulphuric acid containing ice. The amylene is made by heating amyl alcohol with sulphuric acid to vigorous boiling under a reflux condenser kept at 60°- 90° C. to permit the crude amylene to distil, leaving in the flask amyl alcohol and *iso*amyl ether. A better yield of the hydrocarbon can be obtained by a modification, which is fully described in the original, of Ipatieff's method, using alumina as a catalyst.

K. P. McElroy prepares glycols by electrolysing a solution of a chloride under oxidising conditions, the solution being kept saturated with an olefine in presence of an oxygen-carrying catalyst.[106] For the same purpose C. Weizmann and E. G. Bainbridge [107] suspend dichloroparaffins, having the chlorine atoms attached to two different carbons, in water containing aluminium hydroxide, calcium carbonate, borax, or sodium carbonate and heat the mixture in an autoclave at 100°-200° C., when partial conversion to the corresponding glycol occurs.

Aldehydes, Acids, and Ketones.

For the production of formaldehyde by passing methyl alcohol vapour over a heated catalyst G. Calvert [108] has patented apparatus, which can be used for manufacturing purposes or in a small portable form for disin-

[102] K. P. McElroy, U.S. Pat. 1295339 ; *J.*, 1919, 339A, 479A ; B. E. Eldred, Eng. Pat. 113954 ; *J.*, 1919, 512A ; J. M. Moness, U.S. Pat. 1308763 ; *J.*, 1919, 657A.

[103] K. P. McElroy, U.S. Pat. 1308796 ; *J.*, 1919, 658A ; T. and E. H. Kerfoot, J. C. Irvine, and W. N. Haworth, Eng. Pat. 128635 ; *J.*, 1919, 617A.

[104] K. P. McElroy, U.S. Pat. 1315229 ; *J.*, 1919, 847A.

[105] *J. Amer. Chem. Soc.*, 1918, **40**, 1950.

[106] U.S. Pat. 130880? ; *J.*, 1919, 658A.

[107] Eng. Pat. 131628 ; *J.*, 1919, 846A.

[108] Eng. Pats. 126479 ; *J.*, 1919, 511A, and 132120 ; *J.*, 1919, 794A.

fection.   In the second patent, apparatus on a similar plan is described for the general preparation of aldehydes from alcohols by the use of copper gauze as a catalyst.   K. A. Hofmann and H. Schibsted [109] have been unable to obtain more than a 4% yield of formaldehyde by the reduction of formic acid under the most varied conditions, but have had more success with metallic formates, the yield of aldehyde depending on the particular formate used, the control of the secondary reaction represented by the equation $CH_2O = H_2 + CO$, and the avoidance of decomposition of the aldehyde by water.   Zinc formate gives the best yields of formaldehyde and methyl alcohol ; in other cases the metalliferous residues react with the formaldehyde giving methyl alcohol and formic acid or even acetone, furfuraldehyde, and carbon.

Processes for the conversion of acetylene into acetaldehyde as a step in the production of acetic acid and eventually of acetone were fully reviewed in a previous report. [110]   Many patents on this subject, publication of which has been delayed for military reasons, have now become available and some of them give information of considerable interest on details of the methods used, though no new process of importance has been disclosed.   In the hydration of acetylene by the use of a mercury catalyst the latter gradually loses its activity and various methods are suggested for its revivification.   Messrs. J. Crosfield and Sons, Ltd., and T. P. Hilditch have three patents on this subject all depending on the use of oxidising agents.   In the first of these manganic acid, permanganic acid, or a salt of one of these acids is employed, in the second hydrogen peroxide, and in the third various peroxides such as lead peroxide, red lead, cerium dioxide, and manganese dioxide. [111] The difficulty is also dealt with by passing an electric current through the liquid, a special form of apparatus being used to facilitate this operation at any desired time. [112]   In a third method the difficulty is avoided by a vacuum device to ensure rapid removal of the aldehyde, so preventing its action on the catalyst with the formation of byproducts to which the inactivation is attributed. [113]

The hydration of acetylene may also be achieved by passing the gas, largely diluted with steam, through asbestos impregnated with molybdic acid and heated to 600° C. [114]

D. L. Chapman and W. J. Jenkins [115] have isolated a compound of acetylene and mercuric chloride to which they attribute the formula

[109] Ber., 1918, 51, 1398 ; J., 1919, 782A ; cf. J. A. Christiansen, U.S. Pat. 1302011 ; J., 1919, 877A.   [110] Ann. Repts., 1916, 1, 271.

[111] Eng. Pats. 124702, 125926, 131084 ; J., 1919, 388A, 440A, 740A.

[112] Soc. Chem. Ind. Basle, Eng. Pat. 130138 ; J., 1919, 695A.

[113] Comp. des Prod. Chim. d'Alais et de la Camargue, Eng. Pat. 130650 ; J 1919, 740A.

[114] Deutsche Gold- u. Silber-Scheide-Anstalt, Eng. Pats. 107584 and 107585 ; J., 1919, 845A ; cf. Ann. Repts., 1918, 3, 432.

[115] Chem. Soc. Trans., 1919, 115, 847 ; J., 1919, 655A.

HgCl·CH:CHCl and which they regard as the first product of the inter-
action of acetylene and mercuric chloride in acetaldehyde formation.

In the formation of ethylidene diacetate by the action of acetylene
on acetic acid, absorption of the gas is found to be facilitated by the
presence of mercuric acetate and either an aromatic or aliphatic sul-
phonic acid.[116] The diacetate, as already pointed out,[117] yields on
distillation acetaldehyde and acetic anhydride and this action is assisted
by the presence of suitable catalysts such as sodium pyrophosphate,
metaboric acid, and sulphoacetic acid.[118]

According to G. O. Curme [119] acetaldehyde may also be obtained by
passing ethylene into a solution of a mercury salt, the compound
produced being then subjected to anodic oxidation and the acetalde-
hyde formed removed by continuous distillation ; if the oxidation is
prolonged acetic acid is produced.

The oxidation of acetaldehyde obtained in these various ways is
accomplished by air or oxygen, the chief differences in the patents on
this subject lying in the apparatus or means adopted to bring the alde-
hyde quickly and completely into contact with the oxidising agent.[120]

The last stage, conversion of the acetic acid into acetone, is also the
subject of many patents. According to N. V. Sidgwick and B. Lambert,
a practically quantitative conversion into acetone and diethyl ketone
takes place when the vapour of acetic or propionic acid diluted with
steam is passed over pumice stone, on which manganese dioxide has
been deposited, heated to 350° C.[121] H. A. Morton uses for the same
purpose a catalyst containing manganese,[122] and G. O. Curme passes
acetic acid vapour mixed with other vapours over heated, finely divided
iron.[123] A general account of the manufacture of acetone, starting
with calcium carbide, as carried out at the Shawinigan Falls Works in
Canada, has been published by H. W. Matheson [124] and a résumé
of a similar account by E. T. Sterne is also available.[125]

A considerable amount of attention is also being given to the manu-
facture of acetic acid derivatives, including the anhydride, chloride, and
various alkyl esters. A method for the preparation of acid chlorides de-
pends on the reduction of the proportion of sulphur specified in the Gold-

[116] Soc. Chim. des Usines du Rhône, Eng. Pat. 112765 ; J., 1919, 233A.

[117] Ann. Repts., 1916, 1, 275.

[118] Soc. Chim. des Usines du Rhône, Eng. Pat. 131399 ; J., 1919, 846A.

[119] U.S. Pats. 1315543 and 1315546 ; J., 1919, 846A.

[120] H. Dreyfus, Eng. Pat. 130035 ; J., 1919, 739A. Comp. des Prod. Chim.
d'Alais et de la Camargue, Eng. Pat. 130651 ; J., 1919, 739A.

[121] Eng. Pat. 14085 (1915) ; J., 1919, 304A.

[122] U.S. Pat. 1315525 ; J., 1919, 847A.

[123] U.S. Pat. 1315544 ; J., 1919, 847A.

[124] Canadian Chem. J., 1919, 3, 208 ; J., 1919, 793A ; cf. H. W. Matheson,
Eng. Pats. 132557 and 132558 ; J., 1919, 845A, 846A.

[125] E. T. Sterne, J., 1919, 413R.

schmidt method[126] for anhydrides, and proceeds according to one or both of the equations : (1) $2Me \cdot CO_2Na + S + 2Cl_2 = 2Me \cdot COCl + 2NaCl + SO_2$; (2) $3Me \cdot CO_2Na + S + 3Cl_2 = 3Me \cdot COCl + 3NaCl + SO_3$. Sodium may be replaced by other alkali or alkaline-earth metals and acetyl by any other organic acid radicle, e.g. butyric or benzoic. In a subsequent patent it is stated that the absorption of chlorine proceeds more rapidly in presence of 1% of organic or inorganic esters, phenols, ethers, aldehydes, hydrocarbons, or acetals.[127] In another patent the manufacture of acetic anhydride or chloride by the action of chlorine on a mixture of phosphorus and an anhydrous acetate at temperatures below 50° C. is protected. Anhydride is the chief product when chlorine (106·5–177·5 parts) is passed into an intimate mixture of red phosphorus (31 parts) with anhydrous sodium acetate (492- 656 parts) : with less acetate acetyl chloride predominates. The method can also be used for other acid anhydrides and chlorides.[128] A number of processes for the preparation of alkyl esters of aliphatic acids have been patented.[129]

[126] Eng. Pat. 25433 (1908) ; J., 1910, 112.

[127] T. H. Durrans and A. Boake, Roberts & Co., Ltd., Eng. Pats. 128270 and 130399 ; J., 1919, 657A, 739A.

[128] T. H. Durrans and A. Boake, Roberts & Co., Ltd., Eng. Pats. 128282 and 131379 ; J., 1919, 657A, 846A.

[129] G. C Oberfell and H. T Boyd, U.S. Pat. 1302583 ; J., 1919, 554A. A. Boake, Roberts & Co., Ltd., T. H. Durrans, and W. E. Ellis, Eng. Pat. 131088 ; J., 1919, 740A. J. Grolea and J. L. Weyler, Eng. Pat. 131678 ; J., 1919, 794A.
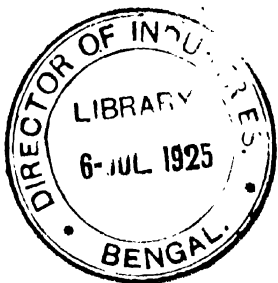
PHOTOGRAPHIC MATERIALS AND PROCESSES.

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THE period under review in the present report, beginning, as it did, practically simultaneously with the cessation of hostilities, has witnessed the publication of results of a large amount of work carried on during the war ; the apparent progress in photographic processes is therefore greater than a strict consideration of the work carried on during the review period would indicate.

The first effect of the peace conditions apparent to an outsider was the reduction in price of sensitive materials from the maximum which they had attained shortly before the armistice. This effect, coupled with the removal of official restrictions on general outdoor photography, was popularly received, and led to an immediate general revival of interest.

So high was the level at which manufacturers kept the quality of materials during the war, notwithstanding the great difficulties which were encountered in securing suitable base materials—glass, paper, and the like that little if any improvement has been noticed in their post-war productions. True, glass has been perhaps not so variable in thickness, and the variety in styles and weights of paper bases perhaps somewhat larger, owing no doubt to the removal of " control," but for average work it is almost impossible to detect whether sensitive material at present on the market is of " pre-war," " war-time," or " post-war " manufacture. The maintenance of such standard can only have been achieved by meticulous attention to details in all stages of the manufacturing operations, and the communication by W. C. Mann[1] indicates the methods which have been adopted to overcome the desensitising effects of salts of copper and iron present in the paper base of the baryta substratum. Cheaper and inferior base can thus be used with impunity.

The advance in price of silver has continued, and should its present price of over 6s. per ounce be maintained a revival of interest in the light-sensitiveness and the adaptability to photographic use of salts

[1] W. C. Mann, *Phot. J.,* 1919, **59,** 184 ; *J.,* 1919, 554A.

of other metals may be expected. Although the actual weight of silver
in the photographic emulsion is relatively insignificant, attention might
be profitably directed to the simplification of the process for its recovery
from used " fixing " baths, into which the bulk of the silver turned out
as an emulsion finds its way. The present process of precipitation as
sulphide, by the action of liver of sulphur, has several drawbacks, not
the least of which is the sludge form of the precipitate. With electri-
city so generally available, it is somewhat surprising that an electro-
lytic process for the deposition of silver as such, has not engaged the
attention of experimenters. Whether thiosulphate would be a suitable
" fixing agent " when such recovery process is contemplated, is doubt-
ful, but the subject is worth attention.

The position with regard to other chemicals used in emulsion making
has become somewhat easier, and apart from the variability in the qual-
ity of gelatin, conditions of supply are reverting towards the normal.
The supply of developing agents is, speaking generally, overtaking the
demand. These circumstances, acting in conjunction with the heavy
stocking by dealers of these substances towards the end of the war,
have led to considerable reductions in prices. The prices demanded are
still high, however, and the consumer has to find what comfort he can
in the fact that the present-day developers are undoubtedly of a vastly
superior quality to those available in the earlier stages of the war.

It cannot be denied that as far as metol and amidol are concerned,
the British manufacturer is supplying material as good as the best pre-
war German products, and, provided economic competition does not
act unduly against him, he should prove himself a serious competitor
on the world's markets. In spite of the popularity both in this country
and America, enjoyed by p-aminocresol, under its many trade names,
there seems to be a considerable demand for the genuine metol. Where
preference for the latter product is shown, it can generally be attributed
to the fact that the base is more soluble and that consequently more
concentrated " stock " solutions can be prepared when a carbonate
is used as the alkali in the developing bath. The preparation of metol
has engaged the attention of many workers during the war, but the
only published results [2] have taken the process little further than it
was detailed in German pre-war literature.

The publication of R. N. Harger's results, the lucid manner in which
they are detailed, and the dedication of his patent to the public must
be accredited as an act worthy of emulation. A study of the patent
literature referring to developing agents leads to the conclusion that
the number of such compounds is legion. The majority of them, how-

[2] R. N. Harger, *J. Amer. Chem. Soc.*, 1919, **41**, 270 ; *J.*, 1919, 234A ; U.S. Pat.
1297685 ; *J.*, 1919, 406A. See, however, A. Lapworth, Eng. Pat. 132555 ; *J.*,
1919, 847A.

ever, are so similar in characteristics that there does not seem to be any advantage in adding to the number already on the market.

The preparation by H. A. Lubs of *p*-aminocarvacrol [3] and its examination as a developer is perhaps justified, as its manufacture would offer an outlet for hitherto waste material.   It is to be regretted, however, that the development characteristics of this and the other compounds prepared were not more fully described, for without careful experimentation and detailed publication of the results obtained, not only is it impossible to come to any just conclusion as to the value of the product, but the formulation of theories on the influence of reactive and subsidiary substituent groups (side chains) is delayed.

The manufacture in this country of dyes suitable for use as colour-sensitisers is still in the hands of a University laboratory staff, although it is to be expected that the publication, in America, of details of the laboratory preparation of pinacyanols and their intermediates [4] will lead to some competition.   Conditions which must be fulfilled in order to render the formation of this quinocyanine possible, have been studied by O. Fischer.[5]   He states that formaldehyde need not be employed, provided air or other oxidising agents be present.   The position in this branch of the art, *i.e.* colour sensitising, is still far from satisfactory.

The communication to the Royal Society by J. W. Nicholson [6] on the distribution of energy in spectra, in which Ewest's method for determination of the extinction boundaries [7] was found to be of great value, is a sorry reminder of the immature condition of affairs.   The band of insensitiveness in the green, which is characteristic of all panchromatic plates, rendered it necessary to refer all measurements, other than those of contiguous or nearly contiguous lines, to a photographic reproduction of the iron arc spectrum in which the distribution of energy has been accurately determined by other means.   Inconveniences attendant on this procedure and the complication introduced by the operation of Schwartzchild's law would disappear if a panchromatic plate having no minima of sensitiveness could be prepared.   The urgency for the production of such a plate increases every day, as our ideas of the composition of matter are becoming increasingly dependent on spectroscopic research.   When the importance of the spectroscope in astronomical research is also taken into consideration, it cannot but be admitted that this is the appointed time for the concentration of the minds of those who are responsible for progress on the problems appertaining to the monochromatic rendering of colour values.

A valuable contribution by F. F. Renwick [8] takes us a step forward.

[3] *J. Ind. Eng. Chem.*, 1919, **11**, 455; *J.*, 1919, 795A.
[4] *Ibid.*, 1919, **11**, 463; *J.*, 1919, 456A.
[5] *J. prakt. Chem.*, 1918, **98**, 204; *J.*, 1919, 199A.
[6] *Nature*, 1919, **103**, 495.   [7] *Phot. J.*, 1914, **54**, 99.
[8] *Phot. J.*, 1919, **59**, 158; *J.*, 1919, 440A.

in the correction of the shortcomings of even the best panchromatic plate at present available, and the issue by the Ilford Company of viewing screens, by means of which a contrast rendering of any coloured view on their panchromatic plate can be observed visually, places a new power in the hands of the photographer. Interposition of a " damping " filter can scarcely be regarded as an ideal operation in spectral photography, however, especially when regions well beyond the visible spectrum, are under investigation a selective absorption of the colloid cannot be disregarded in this case and the only way out of the difficulty is the production of an emulsion, the spectral sensitiveness of which is constant throughout its entire range

The work of W. F. Meggus and C. C. Kiess [9] indicates that success in this matter may be contemplated with assurance, albeit research of a laborious nature will have to be undertaken. The examination by F. Kropf [10] of the colour-sensitiveness of different silver salts emulsified in gelatin is valuable as indicating that little advance is to be expected by the use of salts of silver other than the commonly used halides. No further work on the mechanism of dye sensitisation has been recorded, but it is perhaps worthy of note in this connection, that the new dye, which is the subject of a patent by F F. Renwick and O. Bloch,[11] and also Methyl Violet, which was found to be an effective sensiter by U. Yoshida,[12] are of analogous constitution to already known sensitising dyes, and are definitely known to form lakes with silver iodide.[13]

The characteristic property of lake formation is being studied with other objects in view than that of sensitising, namely, dye-toning of positive images which are to become components of photographs in so-called natural colours. Thus, the conversion of silver images into silver iodide as the preliminary step in the operations has been discarded by J. I. Crabtree [14] and A. Hamburger [15] in favour of the formation of copper ferrocyanide, and by F. E. Ives [16] who prepares a mixed bleached image by treatment with a solution containing one part each of potassium ferricyanide and chromic acid in 120 parts of water. In this latter case use might be made of the absorbed chromic acid which is present in the bleached image for actual dye formation by its reaction upon suitable intermediates.

The application of such toned images to colour cinematography has not so far been considered of much importance.[17] the general preference of most experimenters in this direction appearing to be the,

[9] U.S. Bureau of Standards, Sci. Paper 324 ; J., 1919, 200A.
[10] Phot. Korr., 58, 33 ; J., 1919, 696A.
[11] Eng. Pats. 133769 and 133770 ; J., 1919, 926A.
[12] Mem. Coll. Sci. Kyoto Imp. Univ., 1918, 3, 69 ; J., 1919, 28A.
[13] Compare Ann. Repts., 3, 460.   [14] U.S. Pat. 1305962 ; J., 1919, 602A.
[15] Eng. Pats. 123786 and 123787 ; J., 1919, 304.   [16] J., 1919, 56A.
[17] See, however, Eng. Pat. 119854 ; Brit. J. Phot., 1919, 66, Col. Sup., 38.

easier and simpler plan of projection of the positives of the colour sensation images through suitable screens. In America a fair amount of attention is still being given to the perfection of colour projection in cinematography, and the patent of D. F. Comstock [18] which endeavours, by the use of suitably screened printing lights in making the positives, to correct the false gradation consequent on equal development of negatives made through differently coloured " taking " screens, is indicative of the refinements which are, thought to be worthy of consideration. Comstock's observations appear, however, to be somewhat at variance with those previously referred to. [19]

'The objectionable colour flicker which characterises existing methods of colour cinematography has been studied by J. Shaw, who has been granted a patent [20] for a six-colour process calculated to reduce this drawback. The avoidance of large colour gaps in the sequence of taking and also of projection is the essential feature of the process.

In connection with colour processes not directly concerned with cinematography progress is slow and confined to details. F. E. Ives has taken out a patent [21] for a means of improving the register of images obtained in his process. A single exposure is made using two sensitive emulsions in contact ; one emulsion, insensitive to red, is coated on a two-colour mosaic screen, both colours of which transmit red light, and the other is a plain red-sensitive member on the surface of which a screen is formed by staining with a suitable dye, the composite screen member being towards the lens. From the two-colour composite negative thus obtained pink and yellow positives are printed, using green and blue printing lights respectively, and from the red sensation negative a blue-green positive is prepared. These positives, which preferably take the form of dyed gelatin reliefs, are combined to form the three-colour print. Whilst this process exhibits undoubted advantages over existing methods of colour print production, there does not seem much likelihood of its general adoption for colour transparency work. As recently improved by M. Meugniot [22] the Lumière process is available to the tyro, who can be certain of producing excellent transparencies thereby.

A modification of the Joly process which allows of the production of coloured enlargements has been worked out by S. H. Williams [23] who, in his ordinary practice of the process, obtains the composite print by superposition of bromoil prints.

An entirely new departure in the production of coloured positives is foreshadowed by H. Soar's observation [24] that an ammoniacal

[18] U.S. Pat. 1283087 ; *J.,* 1919, 234A.   [19] *Ann. Repts.,* **3,** 462.
[20] Eng. Pat. 126220 ; *Brit. J. Phot.,* 1919, **66,** *Col. Sup.,* 26.
[21] U.S. Pat. 1306904 ; *J.,* 1919, 602A.
[22] *Brit. J. Phot.,* 1919, **66,** *Col. Sup.,* 37.   [23] *Phot. J.,* 1919, **59,** 88.
[24] Eng. Pat. 127683 ; *J.,* 1919, 554A.

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copper solution containing potassium bichromate when exposed to light
deposits particles the colour of which when viewed by transmitted
white light is the same as that of the light which caused their precipita-
tion.   This process, like that of Lippmann, should not necessitate the
use of a correcting filter during exposure, a circumstance common to all
orthochromatic, panchromatic, or colour processes at present in use.

Dependence on German dyes for making these filters is no longer
necessary, for in addition to the preparation of satisfactory substitutes
in this country, the yellow dye worked out in the Eastman laboratory [25]
shows an absorption with rather sharper cut about 4500 A.U. than
either " Filter Yellow " or Tartrazine.   Filters made with the new dye,
which is prepared by the interaction of phenylhydrazine-p-carboxylic
acid and glucose, have been used with satisfaction by the American Air
Force and exhibit a light-fastness superior to those made with any other
dye except Filter Yellow, to which latter they are only very slightly
inferior.

The part which photography has played in the late war has been one
of prime importance ; in fact, in conjunction with the air arm, it might
reasonably be considered to have been a deciding factor.   The assist-
ance rendered in cartographic survey, in the " spotting " of enemy
positions and movements, in securing definite evidence of the effective-
ness of raids by air, land, and sea, and in propaganda work amongst
those at home, has been eloquently testified to by those best fitted to
express an opinion in the matter.   When it is recollected that in this direc-
tion, perhaps to a greater extent than any other, we were unprepared,
the achievements of the photographic section seem almost incredible.

At the commencement of hostilities a stray photographer was taken
up here and there as an observer ; he used a camera - more often than
not fitted with a lens of enemy origin which required both hands for
its manipulation and with good fortune he brought back some informa-
tion of a more or less reliable nature.

The combined efforts of instructors and workers, of opticians and
camera designers, of plate makers and paper makers, of scientists and
handy-men brought things to such a state of perfection that at the time
of the armistice a veritable swarm of " spotting " and " integrating
eyes " took the air daily with the regularity of the clock and, unmasking
camouflage, returned with information which, placed before General
Headquarters within an hour or two, provided the key to subsequent
operations.   From 40 negatives for the first month's photographic
activity the figure rose to 23,274 negatives and 650,000 prints produced
during October 1918.[26]   This section of the report must include a

[25] Comm. 75, Eastman Kodak Research Laboratories; J., 1919, 118A.
[26] Official Report Phot. Section of the Air Force.   For details of improvements
in apparatus vide Brit. J. Phot., 1919, 66, 139, 238, 293, 299, 309, 396, 411, 428,
440, and Phot. J., 1919, 59, 114.

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reference to the interesting application of a moving film system of record-
ing the movements of the " strings " of a six-string Einthoven galvano-
meter used in circuit with microphones installed in advanced listening
posts. Sound ranging of heavy pieces of ordnance became thereby
a fine art and, although various factors frequently introduced vitiating
errors in the results, the average error of location was as low as 0·5%,
and the average number of definite locations per galvanometer per day
was about 5 — on favourable days a section located 30, 40, and even more
" enemy heavies." This with minimum risk of life and limb.[27]

A very similar device has been employed with success for recording
wireless signals at the American Naval Base, Otter Cliffs, Bar Harbour,
Maine,[28] whereby it is claimed that a single antenna can be used for the
simultaneous receipt of as many as six wave trains, the frequency differ-
ence between any two of which is 225 per second or over. In both of
these recording devices a system of very rapid development is employed
resulting in a sharpness of image and a degree of accuracy of measure-
ment that could not be otherwise attained.

The stimulus given to home manufacturers has led to a complete
eclipse of our late enemies as opticians or photographic dye experts.
Since it was chiefly in these respects that inferiority was most marked
before the war, the competitive position of the allies may now be
regarded with satisfaction.

EMULSIONS AND NEGATIVE PROCESSES.

The progress in colour work and panchromatic photography has
already been recorded.

B. Maklakoff [29] has published details of a process for the preparation
of sensitive emulsions for coating paper in which " cream " replaces the
gelatin. The constitution of the " cream " is not indicated, and it
would be of interest to know whether its contamination with such
substances as lactalbumin, lactose, etc., accounts for its efficiency as
a sensitiser.

The double-coated plate, at one time popular for use in photographing
subjects exhibiting extreme contrast of light and shade, is revived in a
modified form by the Eastman Kodak Company.[30] In this case the
lower emulsion is not used in the making of the negative, the exposure
being so adjusted that only the top rapid film is affected. After develop-
ment, exposure of the lower film is made through the negative and sub-
sequent removal of the top film, followed by development and fixing
in the usual way, gives a positive image.

[27] *Nature*, 1919, **104**, 278.   [28] *Phot. J. Amer.*, 1919, **56**, 233.
[29] *Russ. Phot. Anzeiger*, March, 1916, **90**; *J.*, 1919, 601A.
[30] U.S. Pat. 1303635; *J.*, 1919, 513A.

A very similar device has been patented by C. P. Browning [31] who proposes to coat the double film on a metal plate and, after a series of operations as detailed above, to use the positive as a resist in etching.

The preparation of transparent emulsions, by the use of a large excess of gelatin, suitable for the production of dye-toned images is patented by H. Christensen, [32] whilst workable emulsions of unusually low gelatin content are described by W. Merckens. [33] In this case working viscosity is obtained by treatment with formaldehyde, aluminium acetate or formate. The effect in other directions of the tanning of the gelatin is not stated ; the point is worthy of consideration as it would perhaps give some indication as to whether the groups or other chemical constituents in gelatin, by virtue of which it can be tanned, are concerned in its functioning as a sensitiser.

The rôle played by the gelatin in emulsions is still a matter of conjecture. Whether its physical properties or chemical deportment accounts for its general suitability for emulsion making cannot be stated until further work has been carried out. The patent of H. Müller [34] for the manufacture of emulsions giving steep gradation and in which no noticeable increase in the size of the grain accompanies the usual ripening procedure, protects the peptisation with a solution of pepsin in dilute hydrochloric acid. This patent indicates that some important-ance attaches to the chemical deportment of the sensitiser, for the physical condition is more profoundly affected by such peptisation than is the chemical constitution.

An interesting combination in aqueous solution of a tanning agent (formaldehyde) and an anti-swelling agent (e.g. sodium sulphate) has been patented by A. J. Agnew, F. F. Renwick, and Ilford, Limited, [35] for use as a bath before development in order that the latter operation may be conducted at high temperatures with impunity. It is stated that after the action of this tanning bath the gelatin will withstand aqueous solutions of a temperature as high as 110° C. Apart from this particular application of the solution it should prove useful in such work as that which has recently been conducted on the effect of gravity on light, or in any similar case where negatives are required on which distance comparisons have to be made.

The mechanism of development with organic developers is, so far as the chemical reactions involved therein are concerned, still a closed book. The assumption that during development a dehydrogenation with subsequent condensation occurs, whilst supported by the fact that the ortho and para derivatives only can serve as developers, needs

[31] U.S. Pat. 1285015 ; J., 1919, 118A.
[32] Eng. Pat. 132846 ; J., 1919, 878A.
[33] Ger. Pat. 301291 ; J., 1919, 878A.
[34] Ger. Pat. 313180 ; J., 1919, 878A.
[35] Eng. Pat. 128337 ; J., 1919, 602A.

apparently some modification in view of B. Homolka's [36] discovery that trioxymesitylene (in which the three hydroxyl groups can only be in the meta-position to each other) is an active developer. Whether the theory advanced by Homolka, namely, " The dihydroxy and amino-hydroxy compounds of the benzene series are capable of developing the latent photographic image with the exception of those which, under the conditions of experiment (development), undergo a transformation into the tautomeric aliphatic keto compound " is of general application, only further research will decide.

' The wide variation in the " Watkins factors " of the commonly used developing agents has been considered by J. C. Kingdon [37] who, from experiments in which graduated exposed strips of bromide paper were subjected to the action of diffusing developing solutions whilst sur-rounded by " set " gelatin in test tubes, concludes that the higher factor developers are those of which the critical concentration is low, and vice versâ. In the valuable discussion which followed the communication of these conclusions it was suggested that the Watkins factor was prob-ably a function of the chemical driving force or reduction potential of the developer rather than of its concentration.

It has been concluded by F. Kropf [38] that since a developing solution is turned brown by the addition of either bromine or precipitated silver bromide, but not by precipitated silver, the development of exposed films of silver halide with chemical developers is not due to the separated silver but to the halogen ; this startling conclusion, which appears to have been arrived at from rather meagre experimental evidence, will no doubt receive its due share of attention now that more workers are available.

Machine or tank development, so important in cinematography, is being investigated by the Kodak Research Laboratories' Staff. A com-munication on developer sludge [39] by J. I. Crabtree emphasises the harm-less nature of the deposit of hydrated calcium sulphite which is formed when water containing even as little as 0·025% of calcium sulphate is used for compounding the solution. The sludge is apparently free from oxidised organic development product- a circumstance which is not altogether beneficial in the case of some developing baths, for the accu-mulation of such products in solution undoubtedly tends to check the activity of the " fresh " developer which is added from time to time in strengthening up the bath, and, as would be anticipated from a perusal of Crabtree's remarks on " chemical fog,"[40] causes fog to appear earlier in the process then when freshly prepared developer is employed.

The relative merits of the different developing bases for the prepara-

[36] Phot. Korr., 1914, 51, 256.   [37] Phot. J , 1918, 58, 270 ; J., 1919, 91A.
[38] Phot. Korr., 1919, 56, 141 ; J., 1919, 878A.
[39] Comm. 62, Eastman Kodak Research Laboratories ; J., 1919, 199A.
[40] Amer. Annual of Phot., 1919 ; Brit. J. Phot., 1919, 66, 97.

tion of these standing baths is also being investigated in this country, and during the ensuing year the publication of some important conclusions is to be anticipated.

Attention has again been called to the influence of moisture on the sensitiveness of photographic emulsions by E. Cousin,[11] who has described a simple means of demonstrating it. Unfortunately the phenomenon was not studied quantitatively, and we are not yet in a position to say whether the well-known decrease of sensitiveness which ensues on moistening a gelatin emulsion results from the swelling of the film and the consequent decrease in concentration of the silver halide or whether from " chemical " causes. The fact that over the temperature range $+7°$ to $+64°$ C., a temperature coefficient of 1·06 was found by G. von Dalezki,[42] a figure which is in fair agreement with that previously obtained by several other experimenters, indicates that the amount of chemical action which is effected by exposure to light of a sensitive film is of a very small order ; in view of this fact therefore, the effect of moisture as a function of the " swelling " appears to be worthy of further consideration. The investigation of this and similar problems is complicated by the fact that practically nothing is known as to the order of the absolute inertia, as distinct from the inertia as defined by Hurter and Driffield, of photographic sensitive materials. This absolute inertia might conveniently be referred to Planck's constant as a basis, and it is conceivable also that the results obtained by A. Odenriants,[43] as far at least as they deal with the value of Schwartzchild's constant for differently coloured lights, might be intelligently correlated on the same basis. The determination of the minimal values of time and intensity of illumination which will produce a developable image would not only be of importance in such fields as that of astro-photography, but would greatly facilitate the work of those who are engaged in attempts to increase the sensitiveness of emulsions.

Additional reasons for the adoption of a new unit of inertia are cited in the communication by A. W. Porter and R. E. Slade [14] on the photographic rendering of contrasts, in which it is demonstrated mathematically that it is possible to produce positives exhibiting truthful rendering of the original subject photographed without the image of either negative or positive being confined to the straight line or logarithmic portion of the characteristic curve.

POSITIVE PROCESSES AND AFTER-TREATMENTS.

Improvements in positive emulsions are apparently tending, so far as development papers are concerned, towards the production of papers

[41] *Bull. Soc. Franç. Phot.*, 1919, **6,** 27 ; *J.,* 1919, 118A.
[42] *Russ. Phot. Ber.,* 1916, 155 ; *J.,* 1919, 601A.
[43] *Z. wiss. Phot.,* 1918, **18,** 209 ; *J.,* 1919, 601A.
[44] *Phil. Mag.,* 1919, **38,** 187 ; *J.,* 1919, 600A.

exhibiting greater latitude rather than greater speed, and, although no approach to the printing-out papers in the power of rendering a long scale of gradation has so far been attained, definite progress towards this goal may be reported. Most of the manufacturers now offer a " slow " grade of development paper which, by variation of exposure and development conditions, can be used successfully with nearly every type of negative. This circumstance allows of considerable economy being practised, and when it is stated in addition that it is possible, by minor modifications in the constitution of the developer, to obtain images of a pleasing brown-black colour, thus avoiding the unpleasant " yellow " tones which the " two bath " bleach and sulphide toning of under-developed prints yields, sufficient reason has been given for the growing popularity of this type of paper.

The application of a " non-stress " coating is being more generally adopted than heretofore, as is also some process of tanning the gelatin so that appreciably warm developers may be used without risk of frilling or blistering, and rapid drying on machines of the hot cylinder type may be resorted to.

The formation of blisters or bubbles during the manipulation of gelatin-coated papers has been studied by R. E. Liesegang [45] who concludes that in all cases they are formed by osmotic pressure. The air, which is the prime factor in causing these troublesome defects, is originally to be found imprisoned in the substance of the paper ; by the wetting action of the various solutions it collects between the gelatin and the base, forming convenient minute pockets, the gelatin side of which acts as a semi-permeable membrane when solutions of excessive variations in concentration are employed, and the internal pressure rapidly separates the film from its support.

The opalescence which is frequently noticed when alcohol is used to dehydrate the gelatin of developed gelatin-coated bases is due, according to L. P. Clerc, [46] to calcium bicarbonate, and to a less extent to calcium sulphate, the presence of which arises from the use of hard water in the washing operations.

Amongst the various methods of toning silver prints the so-called " sulphide " process is undoubtedly the most popular, and the investigation by L. P. Clerc [47] on the action of polysulphides on the images formed in various types of emulsion is of considerable interest. His conclusions indicate that the " one-bath " cold sulphide toner which will work with all types of emulsions has still to be discovered.

The use of seleno-sulphuric acid for the modification of sulphide-toned images, producing warmer tones, has been patented by the Eastman Kodak Co. [48] The use of this compound should save many prints

[45] *Kolloid Zeits.*, 1918, **23,** 200 ; *J.,* 1919, 199A.
[46] *Bull. Soc. Franç. Phot.*, 1919, **6,** 85 ; *J.,* 1919, 441A.
[47] *Ibid.,* 1919, 200 ; *J.,* 1919, 741A.   [48] U.S. Pat. 1286890 ; *J.,* 1919, 158A.

which have been regarded as useless on account of the unpleasant tones produced on under-developed images as already referred to.

Another process in which selenium is used, in this case in conjunction with gold for the toning of printing-out paper, has been patented by the Graphikus Ges., Hamburg.[49] It is stated that the tones so produced are similar to those obtained by gold-platinum or platinum toning, and are of greater permanence than those yielded by the former process. The sulphuric acid in the well-known "" reducing " bath containing sulphuric acid and a bichromate, which has been recommended by several manufacturers of colour-screen plates for " reversal " of the negative before its final development as a positive, can be effectively replaced, according to E. Cousin,[50] by sodium bisulphate, provided the proportion of this latter salt does not fall appreciably below 20 grms. per litre of water, the bichromate concentration being of the order of 0·1%. An acid solution of iron alum has also been proposed as a reducer by H. Krause.[51] The so-called " chromium " intensification process is being studied by A. and L. Lumière and A. Seyewetz[52] who, basing their conclusions on the fact that chlorochromates are efficient " bleaching " agents in this process, have advanced a tentative theory of the chemical reactions involved in the process. A critical examination of the theory advanced has been made by R. E. Crowther[53] who, in reiterating his previous conclusions,[54] points out that hydrobromic acid can replace the generally employed hydrochloric acid in the bleaching bath.

The tanning which is produced by the chromic salt when the silver image is caused to reduce a bichromate is taken advantage of by T. P. Middleton[55] in preparing a pigment or carbon paper containing a sensitive silver salt.

After exposure of such paper to light, the silver image is developed and fixed as usual and, after transfer from its original support, is bleached in the usual bromoil bleacher, fixed, and the untanned gelatin removed by warm water. By dyeing the gelatin, precautions are taken in the making of the paper to ensure that the developed silver image is kept near to the surface of the emulsion. The process should prove popular inasmuch as it affords an easy method of producing enlarged " carbon " prints direct from small negatives and further, the transfer to any surface is simplified by application of T. P. Middleton's patented process,[56] in which various gums and resins are coated as a substratum

[49] Ger. Pat. 309447 ; J., 1919, 339A.
[50] Bull. Soc. Franç. Phot., 1918, 6, 26; J., 1919, 118A.
[51] Z. wiss. Phot., 1918, 18, 192 ; J., 1919, 269A.
[52] Brit. J. Phot., 1919, 66, 451.
[53] Ibid., 1919, 709.   [54] See Ann. Repts., 2, 499.
[55] Eng. Pat. 127953 ; J., 1919, 601A.
[56] Eng. Pat. 126149 ; J., 1919, 441A.

between the emulsion and its support. The " true-to-scale " process
in which the tanning action of an insoluble ferric salt is made use of,
has been improved by F. Darel,[57] who adopts the expedient, well known
to the calico-printer, of adding a " sighting " material to the gelatin
composition and so facilitating the subsequent inking operation espe-
cially when light-coloured inks are employed.

RADIOGRAPHY.

Considerable advance has been made in this branch of photography,
due largely to the demands made upon it for the treatment of war
casualties.

The factors which influence " definition " in radiograms have been
studied by A. Lumière,[58] who found that whilst " tubes " differ to a
marked degree in their power of yielding sharp images, the radiant
area of the target undergoes displacement during exposures of three
minutes. The " hardness " of a tube appears to have an influence on
the definition, and for any tube there is a definite hardness below or
above which inferior definition is given. It is concluded that the
improvement in the definition of X-ray photographs is primarily
dependent upon the reduction of the area of the surface impact.

In a mathematical paper by R. E. Slade [59] on contrast and exposure
in X-ray photographs through metals, it is pointed out that a wave-
length of 0.3–0.45×10^{-8} cm., which can be obtained by using a platinum
or tungsten anticathode and the largest possible spark-gap, should meet
all the requirements of ordinary practice.

Only one further result bearing on the sensitometry of X-ray mate-
rials has been published, the attention of experimenters apparently hav-
ing been turned to the improvements of intensifying screens. The
physical characteristics of these screens are dealt with by M. B. Hodg-
son,[60] who points out that crystalline calcium tungstate, giving as it
does, when excited by X-rays, a spectrum extending from about 3600 to
5200 A.U., is the best intensifier with present-day X-ray materials.

The critical minimum for activity of the crystals of calcium tungstate
appears to be very small, for E. E. Burnett [61] prepares a self-contained
radiographic paper by coating an emulsion of calcium tungstate,
in which the crystals must be microscopic, on to paper, subsequently
covering this with an ordinary silver kalide emulsion. If the " speed "
conferred by the screen made and used in this way is commensurate
with that characteristic of the separate screen, this invention should
prove of first-rate importance.

[57] Eng. Pat. 121274; *J.*, 1919, 697A.
[58] *Revue de Radiologie et d'Electrologie* ; *Brit. J. Phot.*, 1919, **66,** 191.
[59] Faraday Soc., April, 1919; *J.*, 1919, 479A.
[60] *Brit. J. Phot.*, 1919, **66,** 191.   [61] Eng. Pat. 125490; *J.*, 1919, 389A.

A. Mutscheller [62] has patented the addition to the emulsion of soluble, transparent, harmless substances which fluoresce under the action of X-rays. In view of Hodgson's findings and also of the fact that greater differentiation in half-tone contrasts is obtainable when the X-rays do not penetrate through the thickness of the emulsion, the incorporation of a fluorescent substance in the film would not be expected to give such valuable results as are obtainable by the calcium tungstate substratum method. There appears to be some advantage in the substitution of cadmium tungstate for barium platinocyanide in the ordinary luminous screen employed in X-ray observation, and although primarily suggested for this purpose, it is stated by P. Roubertie and A. Nemirovsky [63] that the non-permanent white fluorescence can be photographed. An entirely new type of radiation to which the photographic plate is sensitive is the subject of a communication by D. N. McArthur and A. W. Stewart.[64] It was observed that if a plate be exposed behind or in front of a negative, both being in a light-tight wood or cardboard box, for several hours to such heat sources as an electric heater, a sodium or lithium flame, a batswing flame, a Bunsen or Méker burner, or even a beaker of boiling water, a positive print of the negative is obtained on subsequent development of the photographic plate. The "rays" which produce the effect are said to be similar to light rays, in that they may be reflected and refracted. Glass is transparent to them and such substances as ink, seccotine, and metals exhibit different degrees of opacit. The importance of this observation can scarcely be overrated, and it is to be hoped that it will be corroborated by other workers and further investigated by the original observers in the near future.

In concluding this report, one cannot but regret that little improvement has been apparent in the qualities of gelatin available for emulsion making. This constituent of the sensitive emulsion, by virtue of which photography has attained its present position as a most useful servant of the sciences and arts, has been practically neglected by photographic chemists since its introduction. The chemistry of this substance is perhaps of greater importance in the manufacture of photographic materials than it is, for instance, in the leather industry; yet practically the whole of the work published up to the present has been undertaken in the interests, and usually at the expense of those engaged in the manufacture of this latter commodity. The state of affairs which prompted the statement in last year's report [65] that "there are certain chemical differences between different types of gelatin, and even between different batches of the same type, which are more effective than are the physical properties in determining speed, freedom from fog, and

[62] U.S. Pat. 1315324 ; J., 1919, 848A.
[63] Comptes rend., 1919, 169, 233 ; J., 1919, 696A.
[64] Chem. Soc. Trans., 1919, 115, 973 ; J., 1919, 794A.
[65] Ann., Repts., 1918, 3, 465.

such qualities in different types of emulsion. As to the exact nature of these chemical differences there are very few available data . . ." should be altered without delay. The field of research surrounding the chemical deportment of gelatin in photographic operations is obviously so crowded with possibilities in the way of improvements, that the stated intention of the Director of the British Photographic Research Association to take up the matter seriously will be received with much satisfaction by everyone interested in the progress of photography.

EXPLOSIVES : 1914–1919.

By William Rintoul, O.B.E , F.I.C.

Ever since the first use of gunpowder in warfare, sometime in the thirteenth century, explosives have always been the most important of all the agencies employed in warfare, and that nation whose knowledge of explosives was most advanced necessarily possessed advantages over other powers not possessed of this knowledge.

The events of the great war have brought to light the fact that all the participants in it were, at the outset, equipped with a knowledge of explosives of much the same order, and that any superiority in this respect accruing to the belligerent powers during the war was the result of individual progress in the application and use of explosives. For this reason, and as foreshadowed in the Preface to Volume I of these Reports, it was impossible to publish anything with regard to advances in explosives while the war was actually in progress. Now that the fighting is over, however, it becomes possible to review broadly what has been accomplished, although even yet a certain amount of reticence is politic—the existence of the League of Nations notwithstanding.

The period of war was naturally one of great activity in the realm of explosives and allied industries, and it seemed undesirable to limit the present record of progress to the events of the past year. For the sake of completeness it has been decided to review at this time the developments which have taken place from the beginning of the war until the present time. It has been necessary, however, to limit the field covered to explosives themselves, as the advances that have been made in the application and use of explosives would occupy much more space than is here available.

The publication of much information has been withheld during the war and the deliveries of many foreign periodicals were entirely interrupted, and it is only now that these arrears of information are gradually becoming available. This report, therefore, can hardly be exhaustive for the period which it covers, as much of the information which really belongs to that period is not yet obtainable.

HIGH EXPLOSIVES FOR MILITARY PURPOSES.

At the outbreak of war the only explosive used by the British Government as the bursting charge for shell was picric acid or lyddite. It was known that for several years previously the Germans had been using trinitrotoluol for this purpose and the advantages of this explosive were well understood in this country. Although the output of picric acid was rapidly increased and new methods of manufacture were devised and brought into operation, it soon became obvious that the maximum quantity of picric acid which could be produced from the available raw materials would be totally insufficient to meet our requirements, and steps were at once taken to increase the production of existing T.N.T. factories and to equip new plants for the manufacture of this explosive. As the war developed, even these supplies proved inadequate, and ammonium nitrate, of which a very large supply could be made available, was pressed into the service. It was well known that ammonium nitrate, while much too insensitive by itself to initiation of detonation, could be sensitised by admixture with a relatively small percentage of various nitro-compounds. The Research Department, Woolwich, investigated various mixtures with the object of selecting a suitable charge for shell. This investigation finally resulted in the adoption of amatol, consisting of 80% of ammonium nitrate and 20% of T.N.T. As an indication of the enormous quantities of this class of explosive produced during the war, it may be mentioned that the Inspection Department, Woolwich, examined in all 649,000 tons of T.N.T. and ammonium nitrate.[1]

Picric Acid.

In 1911 the technology of the manufacture of picric acid was in a very backward state ; but manufacturers at that time had some excuse to offer for this state of matters, inasmuch as it was recognized that the newer explosive, T.N.T., possessed many advantages over picric acid; and it seemed possible that the British Government might become alive to these advantages to the extent of adopting T.N.T. as the service explosive, in which case the manufacture of picric acid would practically cease. There was little inducement, therefore, to invest capital in the improvement and development of plant which might at any time be scrapped. With the advent of war, however, and the demand for unlimited quantities of all explosives, the situation changed. and it is to the credit of the chemists of this country that the study of this manufacture was at once taken in hand, with the result that it was successfully developed in several directions.

In the "pot" method which had hitherto been used, about one-

[1] Address to the British Association, 1919, by Colonel Crozier, Director of Inspection of High Explosives.

third of the total nitric acid employed was lost by reduction to nitrous oxides and no attempt at the recovery of this was made. The method of dealing with these waste gases was known and it only required the adaptation of existing methods to a particular case to effect a recovery of 95% of the nitric acid previously lost in this way. In the same manner the waste acid from the nitration had usually been discarded. Again, no material difficulty was experienced in adapting known methods for the concentration of such acids to its recovery in an available form. These and other minor changes undoubtedly effected important econo-mies in the manufacture of picric acid by the pot process ; but inasmuch as each pot yields only about 60 lb. of picric acid in one operation, the labour charges in connection with this process must, of necessity, be high. N. Brooke's continuous process,[2] therefore, marks a very definite step in the development of this manufacture. This process is operated as follows : Ordinary phenol is sulphonated by heating for 3 hours at 100° C. with two parts of 95% sulphuric acid and diluted with water to a specific gravity of 1·36. The nitrating vessel consists of a com-partmented baffled acid-proof brick tank about 160 ft. in length. The solution of the sulphonic acid, along with a quantity of dilute sulphuric acid from a previous operation, enters the nitrating tank at one point and 65% nitric acid is introduced through 24 small-bore aluminium jets placed at intervals along the first section of the tank. The nitric acid is added in the proportion of 3·25 parts to one part of phenol. The nitration takes place throughout the first 60 feet of the tank and the temperature at this point does not exceed 102° C. If it falls below this figure, the intermediate sections can be heated by means of cylinders of a suitable material heated internally with steam. The mixture of picric acid and spent acid is cooled as it travels gradually towards the outlet end of the tank, whence it is raised by means of an air lift to a trough delivering into special vacuum filters The picric acid is retained in these filters whilst the dilute sulphuric acid resulting from the process of nitration is collected and submitted to a subsidiary nitration process.[3] This process consists in heating the residual acid by means of closed steam coils. During this heating a further quantity of picric acid is formed from the partially nitrated phenols which are present and the sulphuric acid is concentrated from sp. gr. 1·35–1·37 to sp. gr. 1·45. The acid is again cooled, and, after filtration from the separated picric acid, can be further concentrated to a strength of 92% without difficulty or danger, the recovered acid being used either for the manufacture of nitric acid or for the sulphonation of a further quantity of phenol.

The nitrous fumes evolved during the nitration process are passed

[2] Eng. Pat. 128303 ; J., 1919, 604A. Proc. Brit. Assoc., 1919.
[3] Eng. Pat. 129375 ; J., 1919, 698A.

through water-cooled condensers followed by absorption towers and the recovered nitric acid automatically flows back into the nitration vessel.

The picric acid collected on the vacuum filters is covered with water and allowed to stand for six hours. This water, containing 25% of sulphuric acid and 1% of picric acid, is then run off and concentrated for the recovery of its constituents. The picric acid then receives another water washing, after which it is centrifuged and dried.

As the result of a prolonged run with this plant it was found that a yield of picric acid of 191%, calculated on the phenol, was obtained as compared with 180% which could be taken as a normal yield for the pot process.

The limiting factor in the output of picric acid by the above processes was the supply of raw material in the shape of phenol. The manufacture of synthetic phenol was already an accomplished fact, as it had been made by Messrs. Read Holliday & Co. during the Boer War. A plant had also been installed in the United States by the Semet Solvay Co. at Syracuse,[4] although, for economic reasons, its work had been somewhat intermittent. A considerable quantity of synthetic phenol was produced in this country and employed in the manufacture of picric acid. Another method of overcoming the difficulty of the shortage of raw materials was suggested by various authorities. This process depended upon the conversion of dinitro-chlorobenzene into dinitrophenol and the subsequent nitration of the dinitrophenol to picric acid. The first large-scale plant for the final nitration was erected at the Ardeer Factory of Nobel's Explosives Co., but owing to its destruction, after the nitration of the first charge, by an explosion in an adjacent building, it was transferred to Messrs. L. B. Holliday & Co. Ltd., to whom is due the credit of developing this manufacture on the large scale. The plant which they designed is also available for the direct nitration of phenol to picric acid.

Mention may also be made of the production of picric acid from benzo in the presence of catalytic agents such as mercury. Extensions to the Wolffenstein and Boter patents have been made by D. B. Macdonald,[5] but owing probably to the low yield of picric acid so far obtained by these processes, the method does not appear to have found a technical application.[6] For a similar reason the utilisation of various tree resins like Yacca gum as a raw material for picric acid manufacture has failed.[7]

A certain amount of difficulty was at one time experienced in producing picric acid to conform with the British Government specification in respect of sulphate content; as instances of methods adopted to

[4] *Met. and Chem. Eng.*, 1916, **14**, 144.
[5] Eng. Pats. 126062, 126084, 126675, and 126676; *J.*, 1919, 405A, 480A.
[6] *Chemical Engineer*, 1916, 22.   [7] B. J. Smart, *J.*, 1916, 292.

overcome this difficulty may be cited the patents of N. H. Graesser and E. Mather[8] and of L. B. Holliday and L. G. Badier.[9] The former involves a benzene extraction process for purification. In the Holliday patent water is added to the reaction mixture after nitration in order to produce a high temperature during the dilution. On cooling, the picric acid crystallises out, lead sulphate being retained in the acid liquors.

Trinitrotoluol

The method in use in this country for the manufacture of T.N.T. at the outbreak of war was that known as the three-stage process. The details of operations varied according to conditions. If the aim were to produce T N T, only, as during the war, toluol was converted into mononitrotoluene by means of mixed acid prepared by revivifying, by addition of nitric acid, the waste acid from the dinitrotoluene operation. The mononitrotoluene was converted into dinitrotoluene by adding to it waste acid from a trinitrotoluene nitration and then continuing the nitration by addition of a further quantity of nitric acid. The dinitrotoluene in turn was dissolved in 20% oleum and nitrated to trinitrotoluene by means of strong nitric acid.

In normal times the separation of certain useful by-products of the reactions which occur in the manufacture of T.N.T. is of importance economically, because they constitute valuable intermediate products in the dye industry and consequently command a market of their own. In the three-stage process, as it was worked before the war, therefore, mononitrotoluene was prepared by nitrating toluol by means of a fresh mixed acid. The mononitrotoluene after washing with water and neutralising was subjected to distillation in a vacuum still provided with a dephlegmating column. By this means o- and p-nitrotoluenes were separated. Of these isomers, there is, as a rule, a greater demand for p- than for o-nitrotoluene. The latter was converted into dinitrotoluene by means of a fresh mixed acid and after washing and neutralising was subjected to fractional crystallisation. By this means the 1.2.4-dinitrotoluene was obtained in crystalline form and of considerable purity. The remainder of the crude dinitrotoluene after separation of the 1.2.4-isomer was dissolved in 20% oleum and converted into trinitrotoluene by means of strong nitric acid. Working under war conditions the separation of these by-products could be neglected, particularly as both the o-nitrotoluene and most of the soft dinitrotoluene give α, or symmetrical T.N.T. on nitration, so that there is no loss in yield in carrying them to the final stage.

* Eng. Pat. 126078; J., 1919, 480A. 9 Eng. Pat. 124490; J., 1919, 390A.

This original three-stage process has been modified in various directions during the war. In one modification the nitration operations were reduced to two, the di- and tri-stages being carried out together. This process is employed when the object is to produce T.N.T. only. Toluol is converted into mononitrotoluene by means of a mixed acid made by revivifying waste acid from the trinitrotoluene operation. The mononitrotoluene is then converted direct into T.N.T. in one operation by nitrating it with a strong mixed acid. The dinitrotoluene stage is thus eliminated. It should be noted that in this process the use of oleum is obviated, provided the sulphuric acid employed for the trinitrotoluene mixed acid is of the requisite strength. This was a matter of considerable importance in the early stages of the war when the supply of oleum in this country was strictly limited. To the Research Department, Woolwich, belongs the credit of having worked out the process, which has proved thoroughly satisfactory, and indeed is to be preferred to the three-stage process in respect of yield, output, and quality of product

With this modification there was introduced a method of treatment of the waste acid from the T N.T. stage with the object of recovering as much as possible of the dissolved nitro-compounds and bringing the waste acid to a suitable composition for denitration. It consisted in agitating the spent acid with excess of mononitrotoluene, whereby a certain amount of dinitrotoluene was formed from the residual nitric acid present and practically the whole of the nitro-compounds were removed in solution in the organic medium, which was afterwards used as material for nitration of mononitrotoluene to trinitrotoluene.

The reduction in the number of steps of nitration has been carried even further in the case of the single-stage nitration, where toluene is nitrated direct to T.N.T. in one operation by means of a strong mixed acid. This process does not appear to have been much favoured. This follows from the dangers attendant upon bringing into contact a hydrocarbon of the nature of toluene and a strong mixed acid. Moreover, the advantages to be gained by reducing the number of operations to this extent are not so great as might at first appear. Where, for instance, the mono-nitration is carried out separately, relatively weak acid can be employed, whereas in the single-stage process the mono-nitration must take place with strong acids in order that the final nitration may be complete.

As in the case of picric acid, efforts have been made to devise a continuous process for the manufacture of T.N.T. Before the war the Weiler-ter-Meer type of nitrator was one example of the application of the continuous principle, while the same object was sought in K. Kubierschky's plant.[10] The British contribution to the solu-

[10] Ger. Pat. 287799; *J.*, 1916, 199.

tion of the problem has been•supplied by Messrs. Chance & Hunt,
Managers of H.M. Factory, Oldbury. Their plant is quite different
in conception from any of the hitherto known types; it possesses
a simplicity in design which makes for ease of control and
safe working. The scheme of the plant, which is essentially that
of a counter-current system combined with a displacement process,
was first applied to the washing of trinitrotoluene [11] and later extended
to the nitration.[12]

•A type of nitrator to which reference may be made is the Hough
patent nitrator [13] which has been designed for the nitration to T.N.T.
of large charges of toluene in one operation. A feature of the plant
is the intimate mixing of the nitrating acid and the material to be
nitrated.

Crude T.N.T. prepared by any of the operations referred to is sub-
mitted to a process for the removal of acidity before it is suitable
for issue. Many methods have been employed for this purpose, such
as simple water washing, washing with alkali carbonate or bicarbonate
solution, sulphite or hypochlorite solution. The alkali washing of
crude T.N.T. has always been regarded with a certain amount of
suspicion owing to the undefined nature of the condensation products
resulting from the use of such reagents and the possibility of the forma-
tion of sodium salts, particularly from those isomers or their condensa-
tion products which contain labile nitro groups.[14]

Most of the T.N.T. produced has been used in the crude form, but,
for some purposes, where it is necessary that the T.N.T. should possess
a high sensitiveness to initiation, it is necessary to carry the purifica-
tion still further. This is effected by recrystallising the commercial
product from various solvents such as alcohol, benzene, trichloroethyl-
ene, or from a mixed solvent consisting of alcohol and benzene. By
such treatments, which effect the removal of dinitrotoluene as well
as the β- and γ-isomers of T.N.T., the setting point of the product is
easily raised to 79·5°- 80° C. Another method which has been largely
employed is by washing with sodium sulphite solution. In connec-
tion with the drafting of a suitable specification to govern the purity
of crystallised T.N.T., an investigation has been made into the true
melting point of the pure substance and it has been established, as
80·80°- 80·85° C.[15]

In, view of its bearing on the quality of the trinitrotoluene, it is of
interest to note that the presence of m-nitrotoluene in the crude mixture

[11] Eng. Pat. 125140; J., 1919, 442A.
[12] Chance and Hunt, Ltd., A. E. Holley, and O. E. Mott, Eng. Pat. 124461;
J., 1919, 390A.   [13] Met. and Chem. Eng., 1918, 500.
[14] M. Copisarow, Chem. News, 1915, 112, 283; J., 1915, 1273.
[15] J , 1915, 60.

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of mononitrotoluenes gives rise to β- and γ-isomers,[16] which are objectionable owing to their greater reactivity. The true constitution of these isomers has been established by W. Will.[17] From the purely scientific aspect, it is interesting to note that owing principally to the work of G. Körner, the six possible isomers of trinitrotoluene are now all known.[18] Of these not more than four have so far been isolated from the direct nitration of toluene.

In the crystallisation of trinitrotoluenes the residues, which consist of a mixture of trinitrotoluene isomers and some dinitrotoluene, have been the subject of some work,[16] but no satisfactory application of this by-product appears to have been developed up to the present.

While toluene has formed, in most instances, the raw material for the production of T.N.T., a considerable amount of T.N.T. has been produced from Borneo spirit, a type of petroleum very rich in toluene. This material is nitrated to mononitrotoluene in the usual manner, then washed to remove acids and subsequently submitted to distillation, whereby the non-reactive light oil is distilled off, the residual product being mononitrotoluene. This mononitrotoluene is subsequently nitrated by any of the usual methods. A modification of this process has been suggested by B. J. Flürscheim [20] in which the mononitrotoluene is separated from the paraffins by solution in 96% sulphuric acid, this solution being subsequently nitrated to the tri-stage.

Tetranitroaniline

This explosive, discovered by B. J. Flürscheim,[21] is readily obtained by the direct nitration of m-nitraniline. Although it has not been employed by the British authorities during the war, it undoubtedly possesses great power as an explosive and may be useful for certain specific purposes. Considerable advances have been made in its production in the United States, where the Government has erected a large scale plant in which the safety and practicability of the manufacture has been demonstrated.

The high temperature of nitration specified in Flürscheim's method gives rise to diminished yields, and an investigation of the method has been undertaken by C. F. Van Duin,[22] who nitrates at a temperature as low as $-5°$ C.

[16] M. Giua, *Atti R. Accad. Lincei*, Doc., 1914.   A. E.-Vergé, Eng. Pat. 17128, 1913 ; *J.*, 1914, 890.

[17] *Ber.*, 1914, **47**, 709 ; *J.*, 1914, 376.

[18] Copisarow, *Chem. News*, 1915, **112**, 247 ; *J.*, 1915, 1168.

[19] Copisarow, *loc. cit.*, O. Reuter, U.S. Pat. 1166546; Ger. Pat. 264503; *J.*, 1913, 1088.

[20] U.S. Pat. 1225321 ; *J.*, 1917, 670.   [21] Eng. Pat. 3224/1910.

[22] *Rec. Trav. Chim. Pays-Bas*, 1917, **37**, 111 ; *J.*, 1917, 1030.

Tetryl (Trinitrophenylmethylnitramine).

This substance is more sensitive to initiation of detonation than either T.N.T. or tetranitroaniline, while at the same time it is much less sensitive to shock or friction than is fulminate of mercury. It also possesses in a high degree the property of being able to initiate detonation in less sensitive explosives. It does not readily break down with the production of acidic substances, nor is it particularly liable to form explosive metallic salts. It is therefore very well suited for use as a stepping-up material in the train of events which leads to the detonation of a mass of less sensitive explosives. For example, in the case of the high explosive shell, the shock of impact ignites a small portion of highly sensitive cap composition ; the flash from this ignites pellets of black gunpowder, which in turn cause the detonation of a fulminate cap so placed as to detonate a small column of tetryl, the latter detonation serving to propagate detonation in the main charge of the shell.

The only private plant in this country which was producing tetryl at the outbreak of war was situated in the Ardeer Factory of Nobel's Explosives Co. Ltd. The process employed was similar to that used by the Germans before the war. The raw material used was dimethyl-aniline, which was dissolved in sulphuric acid and nitrated directly by the addition of nitric acid. The resulting tetryl was separated from the residual acids by filtration and was purified by water washing. Where further purification was necessary it was recrystallised from solution in acetone. The advances made in connection with this manufacture during the war consisted principally in improvements in the form of the plant employed. It was at one time considered necessary to carry out the operations of manufacture in glass or silica vessels, but further experience showed that a satisfactory product could be readily obtained from plant constructed of lead throughout.

A method for the production of tetryl from dinitromethylaniline has also been evolved, but this latter process does not as yet appear to have been applied on a large scale. It is of interest to note that monomethylaniline does not give rise to such a good product as dimethyl-aniline, the aminic group of the former apparently not possessing the desirable orienting influence associated with that of the latter.

Hexanitrodiphenylamine.

This explosive, which stands approximately in the same class as tetryl, has been used in considerable quantities by the Germans, but does not appear to have been much employed in this country. It exercises a strong irritant action on the skin and has also the dis-advantage of forming metallic salts. It is not readily produced in a pure condition by the direct nitration of diphenylamine, but usually has to be crystallised after nitration in order to free it from resinous

products.   A method has been evolved' employing as raw materials dinitrochlorobenzene and aniline to form dinitrodiphenylamine, which is subsequently nitrated to the hexanitro-stage.[23]

Hexanitrodiphenyl sulphide, which has been suggested as a bursting charge,[24] has not, as far as is known, been employed extensively (see also p. 570).

Penta-erythritol Tetranitrate.

This substance possesses excellent properties as an explosive, but has' not 'as yet come into common use 'owing to the expense incurred in its production.   It is obtained by the condensation of formaldehyde and acetaldehyde in the presence of lime water, the product of condensation, after purification by alcohol, being subsequently nitrated.[25]

Hexanitro-ethane has been patented as a high explosive.[26]   A thorough examination of it has been made by W. Will.[27]   Its instability at moderate temperatures, together with its cost of production, militate against its general employment.

Dinitrodinitrosobenzene.[28]

This compound, which belongs to the furoxan group, has been employed as a tetryl substitute for various purposes in which the latter found application.

Hexanitrodiphenyl,[29] which may be prepared by the action of copper dust on picryl chloride, has been suggested as a high explosive, but has not come into general use, at least in Great Britain.

Liquid Nitrogen Peroxide Mixtures.

Experiments[30] have been carried out 'with mixtures containing nitrogen peroxide.   Dried nitrogen peroxide gives most powerful explosive mixtures with nitrobenzene and carbon bisulphide.   The optimum mixture of the former is more powerful in the lead block than nitroglycerin, and of the latter than picric acid, but results were not so favourable in the "Stauchprobe."   Nitrogen peroxide-nitrobenzene mixtures have a sensitiveness to shock similar to that of nitroglycerin. The French have used liquid nitrogen peroxide and benzene in compartmented bombs under the name of anilite.   R. Earle[31] also states that benzol and nitrogen peroxide constitute an explosive mixture.

[23] A. Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.*, 1919, 89.

[24] C. Hartmann, Eng. Pat. 18354, 1913.

[25] A. Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.*, 1916, **11**, 182 ; *J.*, 1917, 101.

[26] C. Claessen, Eng. Pat. 24839, 1913 ; Fr. Pat. 463714 ; *J.*, 1914, 276.   G. E. Knöffler, Ger. Pat. Appl. C. 23779.

[27] *Ber.*, 1914, **47**, 961 ; *J.*, 1914, 441.

[28] W. Rintoul and others, Eng. Pat. 16692, 1914 ; *J.*, 1915, 688.

[29] Sprengstoff A.-G. Carbonit, Eng. Pat. 18333, 1914 ; *J.*, 1915, 985

[30] H. Kast, *Z. ges. Schiess- u. Sprengstoffw.*, 1919, 81.

[31] *J. Ind. Eng. Chem.*, 1919, **11**, 924.

A certain amount of confusion exists in the literature with regard to the relative explosive powers of even the most common types of explosives. This is probably due to the insufficient attention paid to the conditions under which the explosives have been initiated. For instance, nitroglycerin placed in a test tube was initiated by silver azide contained in an inner glass tube connected to a fuse. Under similar conditions picric acid, T.N.T., tetryl, and hexanitrodiphenyl-amine did not detonate. A mixture of nitroglycerin and T.N.T. did not detonate when enclosed in a glass bottle using silver azide as above, but a violent detonation occurred when the bottle was placed in a close-fitting tin can. Substitution of a brass detonator capsule for the glass tube containing the azide resulted in detonation when the bottle was placed on a metal support.[32] The physical conditions of the explosive and its confinement have a very marked influence on its detonating properties. It no doubt came as a surprise to many that when the exigencies of war made it necessary, it was possible to use dinitrobenzene without admixture as a shell filling, and even dinitronaphthalene and nitrobenzene can be detonated. The inadequacy of the oxygen content as a guide to explosive value has long been recognised by chemists in the explosives industry and the conditions of internal strain in the molecule and influence of other physical factors are now receiving more attention than hitherto. In tracing a relation between chemical constitution and brisance much valuable work has been done by Stettbacher, for an account of which the original papers should be consulted.[33]

High Explosives for Civil Purposes.

Practically all applications of high explosives under this heading are confined to the operations of blasting in one form or another. The high explosives used for such purposes are known as blasting explosives.

In spite of the enormous demand for high explosives for military purposes during the war, it was necessary to maintain practically a normal supply of explosives for blasting purposes in order that mining operations might not be unduly handicapped. This was done with great difficulty, owing to the interruption of supplies of raw materials and the diversion of many of the usual ingredients of blasting explosives to military uses. The alterations which have taken place in the manufacture of blasting explosives during the period under review have therefore, to a large extent, been of the nature of adapting manufacture to meet new conditions rather than in achieving normal advances in

[32] Stettbacher, Z. ges. Schiess- u. Sprengstoffw., 1919, 137.
[33] Stettbacher, ibid., 1918, 225; 1919, 220, 247; J., 1919, 441A.

technique. Such changes are worthy of record, however, as many
of them will undoubtedly have a permanent effect on the design and
use of blasting explosives.

As an example of the changes introduced to meet new requirements,
it may be mentioned that with the outbreak of war it became impossible
to use potassium salts as ingredients of blasting explosives and steps
had at once to be taken to substitute the corresponding sodium salts ;
but owing to the increased hygroscopicity of the latter and for other
reasons, this was not achieved without a great deal of trouble on the
part of explosives manufacturers, and some sacrifice of properties
hitherto considered indispensable in blasting explosives of high quality.
The difficulty of obtaining ammonium oxalate and the high price
demanded for it rendered this very useful cooling agent in safety blast-
ing explosives practically unavailable, and substitutes had to be inves-
tigated and satisfactory explosives containing them devised. The
demand for nitroglycerin for the manufacture of cordite and the shortage
of glycerin supplies imposed drastic restrictions upon the quantity
of nitroglycerin available for the manufacture of blasting explosives,
and steps had to be taken to develop new compositions containing
lower percentages of nitroglycerin, without interfering more than was
absolutely necessary with the power of the explosives available. For
the greater part of the war the total quantity of nitroglycerin allotted
to blasting explosives was strictly limited and no composition was
allowed to contain more than 50%.

The following compositions may be cited as representing some of
the standard explosives as used before the war and the substitutes
supplied for them under war conditions :

Standard Pre-War Compositions.

	Blasting gelatin.	Gelatin dynamite.	Gelig-nite.	Samson-ite.	Dyna-mite.
Nitroglycerin . . .	90·6	74·1	61·1	59·1	75·0
Nitrocotton . . .	8·8	5·9	3·8	3·4	—
Potassium nitrate .	—	15·7	27·6	18·1	—
Woodmeal . . .	—	4·0	7·2	6·6	—
Ammonium oxalate .	—	—	—	12·8	—
Chalk	0·6	0·3	0·3	—	—
Kieselguhr . . .	—	—	—	—	25·0

War Substitutes.

	50% nitroglycerin gelignite for blasting gelatin, gelatin dynamite and gelignite.	Samsonite 50% nitroglycerin for samsonite.	60% nitroglycerin dynamite for dynamite.
Nitroglycerin	50·0	50·0	38·6
Nitrocotton	2·1	2·8	1·5
Sodium nitrate	38·2	28·6	40·1
Woodmeal . . . • . .	9·4	7·0	18·7
Sodium chloride . . .	---	11·6	—.
Magnesium carbonate . .	0·3	—.	1·1

Where the work was of national importance and it could be shown that gelignite 50% N/G was too weak a substitute for blasting gelatin or gelatin dynamite, special permits were issued authorising the supply of gelatin dynamites of approximately the following composition : Nitroglycerin 71·0, nitrocotton 5·6, sodium nitrate 18·6, woodmeal 4·5, chalk 0·3%.

Nitroglycerin.

II. Hibbert [31] has established the conditions necessary for the formation of both crystalline isomers of nitroglycerin, and particulars are given regarding the solubility, sensitiveness, and crystalline structure. In a later communication [35] he considers that analogies between the phenomena of crystallisation of nitroglycerin, benzophenone, and the cinnamic acids indicate that the two crystalline forms of nitroglycerin are probably chemical isomers which are capable of retaining their individuality in the liquid condition. The freshly prepared liquid consists mostly of the liquid labile form (m.pt. 2^σ C.), though a small quantity of the liquid stable form is also present (m.pt. $13\cdot2^\sigma$ C.). The solid labile form which separates on cooling contains a small amount of the stable form in solid solution and separate crystals of the latter are formed only when the saturation value for them is exceeded. The concentration of the stable form increases on standing. Formulæ are suggested for the two isomers.

H. Hepworth [36] has studied the question from the absorption spectrum standpoint and concludes that the labile and stable forms of nitroglycerin are physical isomerides. Both forms are identical in aqueous solution.

In a discussion of the mechanism of the propagation of explosion through nitroglycerin, R. Becker [37] gives the calculated temperature

[34] Z. ges. Schiess- u. Sprengstoffw., 1914, 9, 83.
[35] Ibid., 1914, 9, 305 ; J., 1914, 984.
[36] Chem. Soc. Trans., 1919, 115, 840 ; J., 1919, 659A.
[37] Z. Elektrochem., 1917, 23, 40 ; J., 1919, 879A.

rises involved by adiabatic compression and by Hugoniot shock compression. The results indicate that the detonation of nitroglycerin is due to the heat caused by the enormous pressure rises.

D. Chiaraviglio and O. M. Corbino [38] point out that the value obtained by Marshall and Peace for the vapour pressure of nitroglycerin at 20° C., viz., $2 \cdot 5 / 10,000$ mm., is considerably lower than that previously found by Marshall, and is near to that found by the authors. They point out that the Langmuir method used by them is much more convenient than that used by Marshall and Peace and is equally reliable. •

C. Girard and P. Iooss [39] give the solubility of nitroglycerin in various oils at 5°, 17°, and 30° C. The solubility in vegetable and animal oils at ordinary temperature is from 10 to 16%. The presence of nitro-compounds increases the solubility considerably.

F. T. Szaffka [40] points out the danger attending the present German method of handling the small quantity of nitroglycerin which separates from waste nitroglycerin acids immediately before denitration, and suggests an arrangement for running such nitroglycerin direct to the after-separating house for treatment in a small separator provided specially for this purpose.

J. G. Baxter [41] has patented a continuous nitration and separation process for nitroglycerin attained by the use of a two-compartmented nitrator having free inter-communication at top and bottom of the compartments, and an attached separator with waste acid and nitroglycerin pipes terminating at the same level.

Heyl [42] regards the phenoldisulphonic acid colorimetric test introduced by Scoville as more suitable than the Kjeldahl method for determining small quantities of nitroglycerin.

Towards the end of 1919 the first two parts of a paper by F. Hofwimmer [43] appeared dealing with the manufacture of nitroglycerin, with special reference to the losses occurring in the nitration and washing processes. He records a series of experiments in which 100-grm. lots of glycerin were nitrated with varying proportions of a water-free mixed acid (HNO_3 46·2%, H_2SO_4 53·8%) and gives the yields obtained and the analyses of the nitroglycerin, residual acids, and wash-waters. From the results it is shown where the losses in glycerin and nitric acid occur under the varying conditions. He states also that the mixing of the residual acids with an equal weight of 20% oleum gives a mixture suitable for the manufacture of nitric acid from sodium nitrate or for the nitration of aromatic hydro-

[38] *Chem. Zentr.*, 1916, II., 726.
[39] *Monit. Scient.*, 1913, 111, 681; *J.*, 1913, 1088.
[40] *Z. ges. Schiess- u. Sprengstoffw.*, 1919, 44.
[41] Eng. Pat. 125091; *J.*, 1919, 442A.
[42] F. W. Heyl, *J.*, 1914, 613.
[43] *Z. ges. Schiess- u. Sprengstoffw.*, 1919, **14**, 361, 381.

carbons. In this way the expensive denitration and concentration processes are avoided.

Again, losses of nitroglycerin in the washing process are diminished by a special scheme of washing which involves first a soda washing and then two water washings, the water from the last two washings being used to prepare the soda liquor for the washing of a subsequent charge. On the large scale this procedure at first gave some trouble owing to sudden evolution of carbon dioxide, causing frothing over, but this difficulty was readily surmounted.

Nitrophenyl glyceryl ether.

Nitro derivatives of phenyl glyceryl ether have been patented[14] for use in explosives. It is claimed that they are free from the defect of instability inherent in the mixtures of the compounds from which they may be regarded as originating, e.g., a glyceryl nitrate and picric acid.

Nitro-isobutylglycerol trinitrate.

F. E. Matthews[45] has patented the use in explosives of nitro-isobutyl-glycerol trinitrate, produced by nitrating nitro-isobutylglycerol.

Nitroglycols and Nitrosugars.

Owing to the readiness with which nitroglycerin freezes and to the shortage of glycerin during the war, considerable attention was directed to the production of the nitration products of the glycols.' Numerous patents have been taken out to cover the use of nitrated ethylene-, butylene-, and trimethylene-glycols.[46] Nitrated sugar is also patented as an ingredient of a blasting explosive together with a nitro-compound, nitroglycerin, woodmeal, and a nitrate.[47] E. J. Hoffman and V. P. Hawse[48] describe the nitration of pure sucrose. The crude product containing 15% of nitrogen was unstable above 30^σ C., but the pure octanitrate, isolated from the crude product by treatment with alcohol, melted at $85 \cdot 5^\sigma$ C. and was very stable and less sensitive to impact than the crude product. The analysis of explosive mixtures containing nitrated sucrose by a polarimetric method is discussed.

Nitrocelluloses.

There is little of outstanding importance to record in the development of the nitrocellulose industry, although the output of this material,

[44] Dinamite Nobel S.A., Eng. Pat. 24352, 1914; J., 1916, 144.
[45] Eng. Pat. 6447, 1914; J., 1915, 453.
[46] U.S. Pats. 1206223, 1213367, 1213369, 1231351, 1307032, 1307033, 1307034; J., 1917, 101, 404, 943; 1919, 604A. Eng. Pat. 106086; J., 1918, 167A.
[47] C. A. Woodbury, U.S. Pat. 1149487; J., 1915, 985.
[48] J. Amer. Chem. Soc., 1919, 41, 235; J., 1919, 234A.

which enters as an ingredient into so many explosives—military and civil—has been on a scale hitherto undreamt of. In the United States, for example, plants have been built capable of turning out 500 tons per day. The concentration of energy on output has been such as to leave little opportunity for development in other directions.

In the early days of the war an opinion was expressed that the cutting off of the supplies of cotton from the Central Powers would result in their early collapse. It is now a matter of general knowledge that this was a mistaken idea and that the enemy were able to fall back upon unlimited supplies of other cellulosic raw materials from which a sufficiently stable nitrocellulose could be produced with little difficulty.

Cellulose prepared from wood was found to afford an admirable substitute for cotton cellulose in the manufacture of explosives; in fact, it has been stated that wood cellulose will be retained as a permanent raw material in preference to cotton.[49] Although it has certain disadvantages compared with cotton, the most important of which is the greater loss of nitric acid entailed on nitration, these are outweighed by the advantages of cheapness, greater purity, and the easier stabilisation of the nitrated product. It seems that sulphite-cellulose manufactured according to the Ritter-Kellner process was almost exclusively used by the Austrian Government during the war.[50] The use of wood cellulose was evidently not unattended with difficulties, as is indicated in a paper by W. Will,[51] in which he describes attempts made to determine the suitability of cellulose for powder manufacture by consideration of the viscosities of solutions in Schweizer's reagent. Complaints had been received from the manufacturers that the tubular powder issuing first from the press and still containing solvent was drier, less plastic, and more readily broken. The finished powders were more brittle and more sensitive to friction than similar powders made from cotton linters or rag cotton. Will comes to the conclusion that the working quality of a gelatinised powder made from wood cellulose depends, to a considerable extent, on factors other than the viscosity of the cellulose or of its nitrate.

C. G. Schwalbe [52] has nitrated various forms of wood cellulose, the main object being to determine the influence of impurities in the wood cellulose on the stability of the resulting nitrocelluloses. The products were all of good stability.

As supplies of cotton were sufficient for the needs of the allied coun-

[49] R. Schwarz, *Z. ges. Schiess- u. Sprengstoffw.*, 1919, **14**, 175; *Oester. Chem. Zeit.*, 1919, **22**, 50, 57; *J.*, 1919, 602A.   C. G. Schwalbe and A. Schrimpff, *ibid.*, 1919, **14**, 41; *J.*, 1919, 555A.

[50] Schwarz, *loc. cit.*

[51] *Z. angew. Chem.*, 1919, **32**, 133; *J.*, 1919, 479A.

[52] *Z. angew. Chem.*, 1914, **27**, 662; *J.*, 1915, 152.

tries, the necessity of developing the use of other raw materials has not arisen. Before the war linters were largely used as the raw material both on the continent of Europe and in the United States? During the war a still lower quality of cotton--hull fibre--was introduced. The hull fibres are the short hairs which remain attached to the cotton seed after the delinting process, and are removed from the seed husk or hulls by attrition in a mill. This fibre, after suitable purification, may be used as a raw material for the production of nitrocellulose.[53]

(*. M. Stine [54] suggests the replacement of nitrocellulose in explosives by nitrated ivory nuts. * Such a material yields a very dense form of nitric ester which, if sufficiently stable, may replace for certain purposes the light fluffy product obtained from cotton or wood cellulose.

Since cotton has not yet been successfully grown in Australia, attempts to prepare nitrocellulose· from a marine fibre (*Posidonia australis*), apparently dredged in large quantities from the sea off the South Australian coast, are of interest. Preliminary experiments suggested that this fibre could be purified on the commercial scale so as to render it suitable for nitration.[55] Further official work has, however, limited the possible use of this fibre for explosive purposes to the production of nitrocellulose for blasting explosives or for the manufacture of " bulk " sporting powders.[56]

Kapok fibre, nearly related to cotton and used to a large extent for filling life-belts on account of its lightness and water-repelling properties, has been stated by W. F. Reid [57] to produce a nitrocellulose which is probably not stable.

W. B. Thomson, W. D. Severn, and G. Twycross [58] claim the employment of the wood of the baobab tree as a raw material for nitrocellulose. Their specification states that this wood has much the same technical qualities as cotton for this purpose and that it is composed of almost pure cellulose and is fibrous to a high degree, the fibres closely resembling cotton fibre both in appearance and in behaviour during nitration.

The importance of the correct determination of the nitrogen content of a nitrocellulose is well known. The usual method of determination is by decomposition with sulphuric acid in the presence of mercury in a Lunge nitrometer; it is now, however, generally accepted that the results obtained by this method, owing to the complex composition of the gases evolved, are inaccurate, and are not even consistent unless

[53] W. F. Reid, *J. Roy. Soc. Arts*, 1915, **63**, 634. E. C. de Segundo, *ibid.*, 1919, **67**, 184.

[54] U.S. Pat. 1143330; *J.*, 1915, 852.

[55] B. J. Smart and P. Pecover, *J.*, 1918, 300т.

[56] J. Read and H. G. Smith, *Inst. of Science and Industry, Commonwealth of Australia, Bull.* 14, 1919; *J.*, 1920, 11A.

[57] *J.*, 1915, 524. Also U.S. Pat. 1302455; *J.*, 1919, 480A.

[58] Eng. Pat. 130665; U.S. Pat. 1302455; *J.*, 1919, 480A.

definite conditions are strictly adhered to in carrying out the determination. The inaccuracies are caused by the evolution of carbon monoxide and dioxide from the organic matter present, the partial reduction of nitric oxide to nitrogen and nitrous oxide and perhaps to ammonia, the solubility of the gases in the sulphuric acid, and so on. Accurate results can, however, be obtained by attention to certain conditions.[59]

It has been shown that the gas obtained by decomposition in the Lunge nitrometer as modified by Horn is purer than that obtained by the Schlösing method.[60] B. Oddo [61] describes a modified form of nitrometer which he calls a " nitrogravimeter." The analysis depends on the determination of the loss in weight caused by treatment of the nitrocotton with a mixture of mercury and sulphuric acid. It is stated to give results which agree well with those of the nitrometer. An improvement of the nitrometer is described by V. Planchon.[62] It is called the manonitrometer. The reaction takes place in an evacuated vessel and the nitric oxide evolved is determined from data obtained from the change of pressure. The accuracy of the nitric oxide determination in c.c. per grm. of sample is about 0·5%. Various advantages are claimed for the apparatus and method. " Nitron " has been successfully used in the precipitation of the nitrate formed on treatment of nitrocotton with caustic soda and hydrogen peroxide. The method was extended successfully to the analysis of nitric esters of mannitol and starch.[63]

Considerable attention is now paid to the determination of viscosity as an additional characteristic of the nitrocelluloses. The factors which give rise to variations in viscosity are obscure. S. Arrhenius [64] contributes a discussion on the limitation of Einstein's formula for the relation between the viscosity and the concentration and states that the logarithmic formula developed by him

$$\frac{d \log n}{dc} = \theta$$

(where n is the viscosity of a solution of the concentration of c grms. per 100 c.c. of solution, and θ a constant) is of greater validity. Deviations from this formula are brought about by dissociation of the solvent or solute molecules or by association between molecules of the solvent and the solute.

[59] E. G. Beckett, J., 1914, 628, and private communication. A. Hervé, Monit. Scient., 1918, 62, 243; J., 1919, 56A.
[60] Köhler and Marqueyrol, Ann. Chim. Anal., 1913, 18, 91.
[61] Gazz. Chim. Ital., 1917, 47, 145; J., 1917, 1195.
[62] Ann. Chim. Anal., 1915, 20, 189; J., 1915, 1031.
[63] W. C. Cope and J. Barab, J. Amer. Chem. Soc., 1917, 39, 504; J., 1917, 473.
[64] Biochem. J., 1917, 11, 112.

S. E. Sheppard [65] discusses the application of Stokes' law to viscosi-
metry, particularly with regard to very viscous solutions such as
those of nitrocellulose, with special reference to the influence of the
wall or boundary of the containing vessel. An empirical formula
correcting for the latter is given. By the aid of this, and a linear
correction for the influence of the total height of the liquid column,
determinations of absolute viscosities of very viscous media may be
made with relatively simple apparatus.

A. D. Conley [66] in an article dealing with the proximate analysis of
nitrocellulose solutions and solvents discusses methods for the deter-
mination of the viscosity of solutions of nitrocellulose. He points out
that it has long been known that two samples of nitrocellulose that
give the same viscosity in wood alcohol do not necessarily give the
same viscosity in amyl acetate. This proves that the boiling point
of the solvent is not the factor which determines viscosity even though
the lower-boiling solvents appear to give the thinnest solutions.

From measurements made in an Engler viscometer, H. Nishida [67]
shows that viscosity measurements can be employed for purposes of
control, and the effect on the viscosity of various factors in the manu-
facture have been determined by this means. These include time of
nitration, percentage of water, composition of acids, treatment of the
raw material, etc. The viscosity of a mixture of nitrocelluloses of
known viscosity may be calculated from the additive law.

A review of the whole subject up to 1913 is given by H. Schwarz.[68]

Reference is made under the section of this report dealing with cor-
dite R.D.B. to work done in this country on the relationship between
the viscosities of the raw cotton and the resulting nitrocellulose (p. 561).

In the analysis of waste acids from nitrocotton manufacture it has
been recognised that the results obtained by the usual methods do not
give altogether a correct idea of the composition, on account of the
impurities present derived from the degradation of the cellulose.
Nitrating acids made up from such waste acids do not give nitrocellu-
lose of the same nitrogen content as those made from fresh acids. It
is stated [69] that one cause of the error is the presence of oxalic acid in
the waste acid, and in a review of the nitrocellulose industry, R. C.
Schüpphaus [70] states that the determination of the oxalic acid has
been a routine operation for a long period in well-conducted factories.

Apart from the Abel heat test, the Bergmann-Junk test seems to
be the principal test adopted to investigate the stability of nitrocellu-

[65] J. Ind. Eng. Chem., 1917, 9, 523 ; J., 1917, 670.
[66] J. Ind. Eng. Chem., 1915, 7, 886 ; J., 1915, 1137.
[67] Caoutchouc et Guttapercha, 1914, 7, 8103, 8200; J., 1914, 476.
[68] Z. Chem. Ind. Koll., 1913, 12, 32 ; see J., 1913, 191.
[69] T. Chandelon, Bull. Soc. Chim. Belg., 1914, 28, 58 ; J., 1914, 334.
[70] J. Ind. Eng. Chem., 1915, 7, 290.

lose.   F. M. Mayrhofer[71] introduces water with the nitrocotton into the decomposition tube in this test and states that changes in rate and amount of decomposition are thus caused which greatly facilitate the diagnosis of instability.

In a paper[72] dealing with the two methods most widely used in Germany for the determination of the chemical stability of nitrocellulose and with a new closed vessel test at 75° C., F. Lenze and B. Pleus give an account of the development of such methods.   Experimental results showed that the 75° C. test gave consistent figures at different times and different places for the same nitrocellulose and that the evolution of red fumes really does indicate the beginning of the decomposition.

In a further communication[73] regarding tests on nitrocelluloses which had undergone storage for various lengths of time and under various conditions, they emphasise the all-round reliability of the new closed vessel test and indicate that the manometer test leaves much to be desired.

A. Hervé[74] discussing the influence of different factors in the nitration of cellulose on the sulphur content, suggests the addition of magnesium chloride to the steaming vat instead of the usual alkaline boil. This salt is claimed to exert a complete saponifying action on the impurities present.   The nitrocelluloses experimented with were of low nitrogen content.

A. Schrimpff[75] discusses the various methods of stabilisation and gives instances of successful results obtained by the use of sodium bisulphite.   He draws attention to the necessity for the more thorough stabilisation of collodion cotton for celluloid.   Another process of stabilisation published in the foreign press involves the use of an alcoholic alkaline solution at 150° C.   J. Duclaux[76] suggests stabilisation by solution in acetone and treatment of the solution with benzene before washing with water.   The impurities remain in the benzene and water.   A suggestion is made by J. Delpech[77] that larger quantities of solvent should be used in the manufacture of French B powder in order that a solution may be obtained which is capable of being filtered through cotton wool under pressure.   In this way specks of lignocellulose and other impurities which form centres of decomposition are removed and a perfectly transparent colloid is produced.   H. Schwarz[78] discusses the chemistry of the cotton fibre, and indications are given of the various ways in which the instability of nitrocellulose used in

[71] Z. ges. Schiess- u. Sprengstoffw., 1918, 13, 425; J., 1919, 603A.
[72] Ibid., 1919, 14, 297.   [73] Ibid., 1919, 14, 377.
[74] Monit. Scient., 1918, 62, 193; J., 1918, 718A.
[75] Z. ges. Schiess- u. Sprengstoffw., 1919, 14, 252, 257.
[76] Fr. Pat. 461785; J., 1914, 222.
[77] Comptes rend., 1919, 169, 437; J., 1919, 795A.
[78] Koll.-chem. Beihefte, 1914, 6, 90; J., 1914, 856.

celluloid manufacture can be diagnosed. The superiority of colloidal antacids over those which appear most promising from an atomistic or molecular point of view is emphasised.

In view of the development of the alcohol dehydration process for nitrocotton, results given for the examination of the soluble products extracted by the alcohol are of interest. F. Langenscheidt[79] states that the nitrogen content varied from 9·4 to 9·6% in the extract obtained with 94% alcohol. Stability tests of the extracted material are also given. Alcohol used for the dehydration of nitrocotton and removed by hydraulic pressure has a higher nitrocellulose content than similar alcohol which has been removed by a centrifugal. Centrifugals are preferred on the grounds of increased economy and suitability of product.

H. N. Stokes and H. C. P. Weber carried out in 1907 very full experiments on the effects of heat on celluloid and similar material, with special reference to the hazards connected with their use and transportation. The results have been published by the U.S. Bureau of Standards.[80] The conclusions of the authors are that celluloid, which term includes pyroxylin plastics, generally does not differ essentially fron nitrocellulose. Decomposition commences at 100° C. and above this temperature the heat of decomposition may raise the temperature above the ignition point. Above 170° C. decomposition takes place explosively as with nitrocellulose. The vapours evolved by decomposition are poisonous and extremely combustible and may be ignited by the heat of decomposition of the celluloid itself.

The Thomson displacement process has been used in this country during the war for the nitration of cellulose for war purposes, but during the later stages the mechanical dipping process introduced from the United States was used for certain products. S. L. Stadelmann[81] gives an interesting account of the various processes and methods evolved in the manufacture of nitrocellulose and nitrocellulose powders in the United States. A. Hervé[82] details results of experiments on the influence of the variation of the percentage of water and nitric acid in the nitrating mixtures on the resulting nitrocellulose. He draws attention to the want of uniformity in nitration obtained when air stirring is used and suggests that this is due to insufficient agitation during nitration. H. Stocker[83] gives the nitrogen content and solubility relationships, in various solvents, of the products obtained by nitration of cotton-wool with mixed acids containing varying proportions of nitric acid and water. The degree of solubility is greatly influenced by the method of manufacture of the nitrocotton and the purity of the solvent. A nitrocotton very soluble in boiling absolute alcohol

[79] Z. ges. Schiess- u. Sprengstoffw., 1914, 9, 54.   [80] Technol. Paper 98, 1917.
[81] Met. and Chem. Eng., 1915, 13, 361.
[82] Monit. Scient., 1918, 62, 193, 241.   [83] Kunststoffe, 1914, 4, 285.

becomes rapidly less soluble as the water content is raised. The time of nitration also influences the solubility. With increasing time of nitration it first rises, then oscillates, and finally falls.[83a] The use of aluminium vessels for nitrating is considered by A. Trillat.[84] It is not possible to lay down any hard and fast rules for the degree of action of the acids on the metal on account of the many variables. Zauner[85] deals with the dangers encountered in the course of manufacture of crude celluloid and with the methods of combating these.

In experiments on the acetylation of nitrocellulose for the production of an acetylnitrocellulose which may serve as an addition to celluloid, Nishida comes to the conclusion that simultaneous nitration and acetylation is the more satisfactory process. The most suitable product obtained in this way was non-inflammable by heating and contained over 9% of nitrogen. It dissolved in chloroform and alcoholic camphor, giving, with the latter, a glutinous liquid readily miscible with nitrocellulose paste.[86] H. Barthelemy states[87] that nitrocellulose is capable of dissolving with partial denitrification in formic acid, especially in the presence of appropriate reagents. There is a substitution of the radicle $H.CO$ for NO_2 and the products are claimed to be considerably more explosive than nitrocellulose of equivalent nitrogen content.

Nitro-starch.

Nitro-starch has never come into general use as an ingredient of explosives owing to the difficulties of stabilising the product. G. Jones[88] states that these difficulties having been overcome, it is now one of the safest of all explosives to handle and has found important military uses. It was formerly manufactured from tapioca, but is now obtained of superior quality and more economically from corn starch. C. E. Waller[89] has patented two explosive compositions containing nitro-starch.

Gelatin Explosives.

Since the introduction of blasting gelatin and gelignite by Alfred Nobel about the year 1887, gelatinous blasting explosives have always been manufactured by incorporating the ingredients in mixing machines by means of a hot water jacket. One of the results of a prolonged and systematic research into the gelatinising properties of various substances, carried out by Nobel's Explosives Company, has been the discovery that certain classes of chemical compounds possess the pro-

[83a] H. Schwarz, Caoutchouc et Guttapercha, 1914, 11, 7964 seq.; J., 1914, 744.
[84] Bull. Soc. d'Encour., 1915, 132, 547; J., 1915, 874.
[85] Z. Gewerbehygiene, 5, 199.
[86] H. Nishida, Kunststoffe, 1914, 4, 141; J., 1914, 476.
[87] Caoutchouc et Guttapercha, 1917, 14, 9274.
[88] J. Ind. Eng. Chem., 1918, 10, 784.
[89] U.S. Pat. 1305845 and 1305846; J., 1919, 604A.

perty of accelerating the solvent or gelatinising power of nitroglycerin.[90] To take a simple case, it has been found that the addition of as little as 0·08% of formanilide to the ingredients of blasting gelatin increases the gelatinising power of the nitroglycerin to such an extent that well-gelatinised blasting gelatin can be produced by merely incorporating the ingredients at the ordinary temperature. It has long been known that the sensitiveness of explosives to ignition by friction or shock increases with the rise of temperature: One great advantage to be obtained from the application of the new discovery is, therefore, at once evident—the possibility of conducting the manufacture of gela-tinous explosives in the cold instead of at an elevated temperature enormously reduces the dangers of explosion incident to this manu-facture. This new method of manufacture has now been exclusively adopted at the Ardeer' Factory of Nobel's Explosives Company, and with the continued use of this process it has been found to possess important advantages in other respects. The reduction in temperature of incorporation does not indicate the full measure of the accelerating power of the new ingredients, as, even at the lower temperature, it has been found that the time taken to obtain the required degree of gelatinisation is considerably less than by the old method of hot gelatinisation. This results in an increased productive capacity for any given plant. It has also been found that the sensitiveness to initiation of the explosives produced by the method of cold gelatinisa-tion is superior to that produced by the old process. Gelatinous explosives gradually lose their sensitiveness to initiation when kept for any length of time, and the warmer the climate in which they are kept the more readily does this fall in sensitiveness manifest itself. Explosives made by the cold gelatinisation process have been found to retain their sensitiveness for a longer period than those prepared by hot gelatinisation. This factor is an important advantage from the point of view of the actual application of explosives. The accel-erators now used possess the additional property of stabilising high explosives of the nitric ester type. Consequently the chemical stabi-lity of these explosives should be somewhat increased, though this is not generally a matter of great importance, as the life of such an explosive is measured, not by its chemical stability, but by the length of time during which it retains its power of being initiated by a service detonator.

This new type of explosive possesses therefore several material advantages, and in no single property has it been found to be inferior to similar explosives made by the original process.

D. Chiaraviglio and O. M. Corbino [91] discuss the formation of the nitro-

[90] W. Rintoul, D. Cross, and Nobel's Explosives Co., Eng. Pats. 14655 and 14656 of 1915, and 126056; J., 1919, 340A, 513A. Arms and Explosives, 1919, 126.
[91] Z. ges. Schiess- u. Sprengstoffw., 1915, 10, 156; see J., 1915, 637.

glycerin-nitrocellulose colloid.   On placing nitroglycerin and nitrocellu-
lose separately in an evacuated vessel kept at a uniform temperature of
30° C., the nitroglycerin was absorbed by the nitrocellulose to an extent
depending on the type of nitrocellulose and the duration of the experi-
ment.   A rise of temperature was observed on dropping nitroglycerin
on to guncotton *in vacuo*.   The decision as to whether the explanation
should have a chemical or physical basis is postponed.

W. A. Hargreaves [92] discusses the nature of blasting gelatin.   He
considers it to be a colloidal solution of nitroglycerin in nitrocotton
mixed with free ungelatinised nitroglycerin.   Insensitiveness may be
avoided by reducing the nitrocotton content.   After storage for one
year results originally obtained with a No. 6 detonator can only be
duplicated if a No. 7 detonator is used.   The explosion wave following
detonation of blasting gelatin is transmitted by free ungelatinised nitro-
glycerin and only imperfectly or not at all by the jelly.   If there is
no free nitroglycerin, or if the particles of the nitroglycerin are far
apart, the blasting gelatin becomes insensitive.   E. Weiskopf,[93] how-
ever, states that it is unnecessary to have liquid nitroglycerin in the
explosive in order to obtain high sensitiveness, as nitroglycerin itself
is incapable of transmitting the explosion wave.

H. Hibbert [94] finds that when blasting gelatin is frozen the nitro-
glycerin separates in the labile crystalline form.   The greater sensitive-
ness to shock of frozen blasting gelatin compared with frozen gelatin
dynamite is probably due to the tendency of the labile form of nitro-
glycerin to change to the stable form with the liberation of energy.   In
the case of gelatin dynamite the nitroglycerin separates in the form
of the higher-melting stable derivative owing to the presence of sodium
nitrate and other substances.

E. A. Mann and T. N. Kirton [95] report that, in an investigation of the
causes of the inertness in gelatinous blasting explosives, D'Autriche
tests were carried out on gelignites containing sodium and potassium
nitrate, gelatin dynamite, and blasting gelatin.   The gases obtained
in the workings were also analysed.   Indications were obtained that
sodium nitrate explosives develop inertness more rapidly than potas-
sium nitrate explosives.   The use of No. 7 and No. 8 detonators instead
of No. 6 detonators did not cause higher results to be obtained in the
D'Autriche test.   The study of nitrocotton solutions in amyl acetate
indicates that under certain conditions of temperature, etc., some mole-
cular change takes place in the nitrocotton constituent of the explo-
sives, thereby causing insensitiveness.   Results are given of D'Autriche

[92] *J.*, 1914, 337.   [93] *J.*, 1914, 340.
[94] *Z. ges. Schiess- u. Sprengstoffw.*, 1914, 9, 322 ; *J.*, 1915, 984.
[95] "*Investigations into the Development of Inertness in Industrial Explosives of
the Nitro-compound class*," 1918; *J.*, 1919, 848A.

tests carried out by Nobel's Explosives Company of blasting explosive confined in the bore hole, the velocity of detonation obtained unde these conditions being practically the same as with the unconfined explosives.

W. S. Simpson [96] gives results of practical tests of blasting gelatin, ree gelatin, and gelignite on the Rand, showing that their relative blasting efficiencies agreed closely with their comparative ballistic strengths He deprecates the use of 40% Ligdyn•as a primer for blasting gelatin and reef gelatin. This opinion is supported by W. Cullen and B. H Lindhorst.[97]   P. B. MacDonald,[98] however, holds the opinion that high detonation velocity primers are advantageous.

Various patents have recently been taken out for specific composi tions suitable for use as gelatin explosives. A. E. Vergé [99] claims a composition consisting of dinitrotoluene gelatinised with nitrocottor and incorporated with oxidising salts with or without nitroglycerin S. Adde [100] has put forward a low-freezing plastic explosive containing fluid nitro-derivatives of xylene or cumene or mixtures of these togethei with nitrocotton and other ingredients with or without alcohol or nitroglycerin. C. I. Tisell [101] has protected the use of aluminium powder containing ferrosilicon of high silicon content in explosive mixtures comprising nitrohydrocarbon, oxygen carriers, and combus-tibles, plasticity being secured by admixture of nitrocotton.

Non-Gelatinous Explosives.

C. A. Woodbury [102] claims an explosive of the ammonium nitrate class, the essential feature of which is that the ammonium nitrate is present in relatively large particles in order to reduce the velocity of detonation and obtain an explosive of less shattering character.

G. F. Bradley [103] has patented compositions of explosives which may be prepared in plastic, semi-plastic, or granular form, consisting of ammonium nitrate, trinitrotoluene, trinitroxylene, and aluminium. J. Hargreaves and others [104] have attempted to reduce the sensitiveness of explosives of the Amatol type in a composition containing ammo-nium nitrate, T.N.T., and ulmic anhydride.

W. Kummer [105] states that mixtures of ammonium nitrate and 32% sodium mononitrophenate, or 25% mononitrophenolsulphonate salt, or 25%, 22% and 20% of dinitrophenol salt have been found to be suitable explosive compositions.

Sabulite, an ammonium nitrate explosive containing calcium silicide

[96] J. S. Afr. Inst. Eng., 1916, 120.   [97] Ibid., 37.
[98] Min. and Sci. Press, 1916, 788   [99] Eng. Pat. 17205, 1913 ; J., 1914, 943.
[100] Eng. Pat. 112618 ; J., 1919, 513A.   [101] Eng. Pat. 116890 ; J., 1919, 513A.
[102] U.S. Pat. 1124679 ; J., 1915, 250.
[103] Eng. Pat. 126698 ; J., 1919, 514A.   [104] Eng. Pat. 131380 ; J., 1919, 795A.
[105] Montan. Runds , 1919, 11, 2.

and T.N.T., has been tested in British Columbia.[106] It was subjected
to temperatures of 258° F. and −75° F. without affecting its properties.
It is claimed to be two-thirds more destructive than dynamite and to
give no poisonous fumes on explosion. This explosive has apparently
failed, however, after numerous and exhaustive tests made by the
Anaconda Copper Mining Co.[107] Under favourable conditions it is
of great strength, perfect safety, insensitive to shock, friction, fire, or
frost, while the fumes are harmless. Under wet conditions, unfortu-
nately, it is absolutely ineffective.

In the amended German railway regulations[108] compositions are
given of numerous ammonium nitrate explosives.

A. Wogrinz[109] gives a method for the determination of the aluminium
in ammonal. The ammonium nitrate and nitro-compound are first
removed with water and chloroform and the residue of carbon and
aluminium decomposed by a 50% solution of potassium hydroxide.
The maximum error is about 0·5% of the aluminium present.

In an article[110] dealing with blasting explosives for industrial work
in war time, A. Spielmann states that chlorate explosives have been used
successfully in place of ammonium nitrate explosives where dangers
from firedamp and coal dust are absent. Suitable chlorate mixtures
have also been developed for replacing black powder in quarry work
where shattering must be avoided.

J. C. Thompson[111] also discusses the efficiency of chlorate explosives
and shows that permissible explosives of the class containing potassium
chlorate have not been a success, as not only is an explosive containing
chlorate more sensitive as a rule to percussion and friction than those
in which the oxygen carrier is a nitrate, but it is also more violent in
its action. Moreover, chlorate is more liable to crystallise on the
surface of the explosive, a condition which gives rise to a considerable
increase in sensitiveness.

C. Girard and P. Iooss[112] propose an explosive which is prepared by
moistening gelatin with water and incorporating a slight excess of
chlorate or perchlorate. The gelatin is then rendered insoluble by
the addition of a small proportion of formaldehyde and stoving at
110° C. The mixture is granulated and the grains treated with castor
oil containing dissolved nitro-compound. After further incorporation
the mixture is dried at 100°.

'Merkurit I[113] consists of 88% potassium chlorate and 12% tar oil.
In Merkurit II 20% of the chlorate is replaced by perchlorate. Wetter
Albit[114] consists of a mixture of chlorates and nitroglycerin with mono-

[106] R. E. Mansfield, *U.S. Cons. Repts.*, 1914, 1641.
[107] *Eng. Rev.*, 1915, 47.
[108] *Z. ges. Schiess- u. Sprengstoffw.*, 1918, 25, 105; 1919, 163, 196, 259, 340.
[109] *Ibid.*, 1919, 64; J., 1919, 927A.   [110] *Ibid.*, 1916, 89.
[111] *Coal Age*, 1919, 16, 94.   [112] *Monit. Scient.*, 1913, 111, 684.
[113] *Z. ges. Schiess- u. Sprengstoffw.*, 1919, 196,   [114] *Ibid.*, 1915, 69, 129.

or dinitro aromatic hydrocarbons, etc. Gesteins Koronit [115] contains chlorates, nitronaphthalene, and woodmeal with or without addition of nitroglycerin and oils. Chlorat Baldurit [116] also contains chlorates and aromatic nitrohydrocarbons, etc. Perazite [117] consists of a mixture of alkali perchlorate, ammonium nitrate or alkali chlorate, aromatic nitrohydrocarbons not more dangerous than dinitrotoluene, etc.

W. J. Hoynes [118] prepares an explosive by feeding a powdered mixture of potassium chlorate and sugar into a rotating drum in a moist atmosphere whereby the materials cohere into spherical grains. F. R. and J. G. Burrows [119] claim a composition consisting of 6% ammonium perchlorate, 56% potassium nitrate, 18% water-cooled aluminium, 18% T.N.T., and 2% paraffin. Aktiebolaget Carlit [120] suggests the improvement of ammonium perchlorate explosives by the addition of less than 1% of alkali chlorate in order to increase sensitiveness and velocity of explosion.

A. J. Marin [121] has put forward a number of non-nitroglycerin compositions which are claimed to possess certain advantages. In his first patent he describes explosives containing ammonium perchlorate, sodium nitrate, and trinitronaphthalene compressed wet to such an extent that when dried they give a density of 1·45-1·6. He also claims [122] a plastic blasting composition containing ammonium perchlorate, sodium nitrate, aromatic nitro-hydrocarbons, and guanidine nitrate, to which he adds trinitronaphthalene, with the object of preventing setting. Another patent [123] is for an explosive containing 66-71% of a mixture of ammonium perchlorate and sodium nitrate and 34-29% of a mixture of tetra- and trinitronaphthalenes compressed wet to give a dry density of 1·33-1·62. He finally [124] claims the use of a wet mixture of ammonium nitrate and sodium perchlorate which he states produces a double salt. The product is mixed with trinitrobenzol, moulded into cartridges, and dried.

F. G. L. Johnson [125] patents a plastic explosive containing ammonium perchlorate and potassium perchlorate, preferably in equal parts, to which he adds 17-18% of molten wax. W. Blackmore [126] proposes a perchlorate explosive containing anthracite and carborundum A. E

[115] Z. ges. Schiess- u. Sprengstoffw., 1918, 252.
[116] Ibid., 1918, 252.   [117] Ibid., 1919, 340.
[118] Eng. Pat. 6755, 1914; J., 1914, 1227.
[119] Eng. Pat. 11562, 1914; J., 1914, 1227.
[120] Eng. Pat. 112417; J., 1918, 637A.
[121] Eng. Pat. 108853; see J., 1919, 390A.
[122] Eng. Pat. 121294; J., 1919, 698A.
[123] Eng. Pat. 129036; U.S. Pat. 1297213; see J., 1919, 390A.
[124] Eng. Pat. 131388; J., 1919, 795A.
[125] Eng. Pat. 125128; J., 1919, 442A.
[126] Eng. Pat. 125663; J., 1919, 443A.

Charbonneaux [127] prepares an explosive by mixing 5 parts of ammonium naphthalene sulphonate with 10 parts of potassium perchlorate and 1 part of finely powdered potassium permanganate. A. B. Cole [128] has a patent for the use of a mixture containing 25% sugar, 30% potassium chlorate, 22% coal, 20% sodium nitrate, 2% alcohol, 0·5% each of lampblack and potassium permanganate. R. G. Smith [129] has two patents for the use of zinc dust with a mixture of ammonium and alkali perchlorates together with sulphur or suitable carbon compounds and preservatives of the zinc. According to W. C. Wain's patent,[130] a mixture of castor oil, linseed oil, and petroleum is nitrated with funfing nitric acid and the nitro-compound so produced is used as the saturating liquid in a chlorate explosive of the Sprengel class. I. B. T. von Tarnow [131] has a patent for an explosive consisting of powdered aluminium, nitro-hydrocarbon, and ammonium perchlorate, with or without nitrocellulose, nitrates, sawdust, paraffin, etc. Dynastite is the name given to an explosive by G. A. Rauzieres.[132] According to his patent it is composed of 94 parts potassium chlorate and 6 parts barium nitrate, dipped in nitrotoluene oil.

Liquid Air or Oxygen Explosives.

As has already been pointed out, the conditions brought about by the war necessitated the restriction of the usual explosive ingredients used in blasting explosives. This state of affairs naturally directed increased attention to the possibilities of liquid air explosives. Especially was this so in Germany. Early in 1914 M. Claude and D'Arsonval [133] had adapted liquid air for commercial use as an explosive. The cartridges were bags filled with a special kind of lampblack and were soaked in liquid air just before use. It was claimed that the power of this explosive was equal to that of dynamite. Powdered aluminium [134] also was used with excess of liquid air, but as the products are not entirely gaseous, the efficiency of such an explosive was low. Tests carried out at the Pittsburg Laboratory [135] showed that a mixture of liquid oxygen (85%) with carbonaceous and absorbent material was equivalent in strength to 40% dynamite. In comparative experiments [136] with liquid air explosives, gelatin dynamite, and Aldorfit, the explosive force of the liquid air explosive exceeded that of the

[127] U.S. Pat. 1093767 ; J., 1914, 569.
[128] U.S. Pat. 1126401 ; J., 1915, 303.
[129] U.S. Pats. 1243231 and 1243351 ; Eng. Pats. 2169 and 2172, 1915 ; J., 1917, 1290.
[130] U.S. Pat. 1240272 ; J., 1917, 1149.
[131] Fr. Pat. 465082 ; J., 1914, 569.   [132] Fr. Pat. 465718 ; J., 1914, 614.
[133] Engineering, 1914, 331.   [134] Engineering, 1915, 100.
[135] Colliery Guardian, 1919, 481.
[136] M. Enderli, Z. ges. Schiess- u. Sprengstoffw., 1919, 153.

others, but in practice evaporation causes a considerable diminution in power.

Oxyliquit has been successfully applied in potash and coal mines.[137] The cartridge composition was modified by the addition of salt or water to the lampblack so as to prevent the flame of explosion from igniting the firedamp or coal dust. In stone quarries oxyliquit has not been so successful.[138] Pabst [139] gives an exhaustive list of mines, quarries, etc., in which liquid air or oxygen has been adopted. Exceptional difficulties were experienced in adapting liquid air explosives for use as safety explosives in coal mines. With cartridges containing salt as safety ingredient, the loss of sensitiveness to detonation due to evaporation was very rapid, and ultimately the detonator merely ignited the cartridge, thus causing gas ignitions. However, an important advance has been made by the introduction of special detonators which are so constructed that they are only effective when moistened with liquid air, so that when the cartridge has lost so much of its liquid air by evaporation as to become insensitive the detonator becomes ineffective at the same time. Ordinary detonators, of course, become insensitive at these low temperatures. Pabst gives an account of gallery tests carried out in 1917 with a liquid air explosive, Sprengluft No. 2, at the Beuthen safety explosives testing gallery, in which the explosive was safe in gas at a charge of 500 grms.

Although the explosive power of liquid air increases with the proportion of oxygen, yet the cost of production by the older methods increased even more rapidly, making it economical to use liquid air containing 50% oxygen. By the recent Mewes method of alternate vaporisation and condensation the cost of the fractionation of the gases has been reduced so that liquid air containing a high percentage of oxygen now becomes the more economical.[110]

Liquid air is unsuitable for use as an explosive in shaft sinking owing to the liability to formation of carbon monoxide through delay in firing.[141] It is, however, very suitable for blasting compact rock and in coal mines.[142]

The adoption of liquid air explosives in Upper Silesia has become so general that the Oberschlesische Sprengstoff-Ges. do not anticipate a return being made to the older explosives for some time,[143] and two Swedish Explosives Companies are at present erecting seven plants in Sweden for the production of liquid air for use in mines.[144]

[137] Sci. Amer. Suppl., 1918, Oct. 26, 1918.

[138] Bull. Soc. d'Encour., 1918, 78.

[139] "Flüssiger Sauerstoff und seiner Verwendung als Sprengstoff in Bergbau," 1917.

[140] Z. Sauerst. u. Stickstoff-Ind., 1915, 41.

[141] H. Joosten, Colliery Guardian, 1919, 91.

[142] A. Schwarz, Z. ges. Schiess- u. Sprengstoffw., 1919, 32.

[143] A. Schwarz, ibid., 1919, 92.   [144] Z. angew. Chem., 1919, 635.

Details of the comparative costs of liquid air explosives and the older explosives are given by Pabst [145] and also in a review [146] which gives tables showing the total cost of blasting by liquid air at Sachsen-Weimar and Wintershall. At Sachsen-Weimar the economy from the use of liquid air enabled the cost of the plant to be paid off in 22 months, but at Wintershall there will probably be, in the future, nothing to choose between liquid air and the older explosives.

Permitted Explosives for use in Coal Mines.

After March 15, 1914, the new permitted explosives which had passed the Home Office Gallery Test at Rotherham, replaced, with one exception, the old permitted explosives which had passed the Woolwich test. [147] This exception was Bobbinite, which, as the result of a special commission, had been retained on the list, but under a separate schedule and only for coal getting in non-gassy mines. By the above date no less than 35 different explosives had passed the revised test. These explosives were comprised roughly of the following classes :

(1) Ungelatinised explosives :
    (a) Ammonium nitrate-nitroglycerin compositions.
    (b)   ,,   ,,   -nitro-compound   ,,
    (c) Modified carbonites.
(2) Gelatinised explosives of the potassium perchlorate-nitro-glycerin class.

During the next few months numerous compositions passed the test, but the only ones showing distinctive features were Duxite and Arkite No. 2, which were gelatinous explosives similar to Dynobel, but containing sodium nitrate and potassium nitrate respectively, and Neonal No. 1 and Super-rippite which were of the true gelatin type possessing the great advantage of high density.

Soon after the beginning of the war there was, as has been said, a general shortage of raw materials, but more especially of potassium salts and ammonium oxalate. Attempts were made to use sodium nitrate in place of potassium nitrate or perchlorate, and the explosives containing the latter salts were gradually withdrawn from the market. After a short time sodium chloride became practically the only safety ingredient with, in some cases, a small admixture of ammonium oxalate. This led to the introduction of the sub-stitute explosives such as the Viking Powders, Thames Powder No. 2, Britonite No. 3, and Dynobel No. 2.

In consequence of the shortage of glycerin, the Director of Propellant Supplies prohibited the manufacture of all permitted explosives con-taining more than 15% of nitroglycerin as from February 20, 1916.

[145] Loc. cit.   [146] Z. ges. Schiess- u. Sprengstoffw., 1919, 240.
[147] Explosives in Coal Mines Order, Feb. 2, 1914.

This practically limited the field to ammonium nitrate explosives, and this state of affairs remained until the end of 1918.

Nothing of importance has been done as regards safety explosives since the Armistice. Two more gelatin explosives, Samsonites Nos. 2 and 3, similar to Super-rippite, have been added to the Permitted List, and some compositions have been re-tested at Rotherham in connection with the transfer of their manufacture to other factories. Full details of the Permitted List compositions are to be found in the Explosives for Coal Mines Orders for 1913–1919.

During 1919 the number of explosives on the Permitted List had reached 78. Seeing that many of these explosives were no longer manufactured and had been superseded by improved explosives, a review of the list was made as the result of an arrangement between the explosives manufacturers and the Home Office. The Explosives in Coal Mines Order of November 14, 1919, containing this revised list of 34 explosives came into force on January 1, 1920. A. Marshall [148] discusses the various types of permitted explosive and E. de B. Barnett, [149] from a comparison of the compositions and the results of the tests, draws certain deductions, but at the same time points out many curious anomalies.

Patents have been taken out to cover the composition of Super Excellite No. 3, [150] containing ammonium nitrate 60%, nitroglycerin 9·5%, collodion cotton 0·5%, starch 4%, sodium chloride 15%, ammonium oxalate 10%, castor oil 1% ; and to cover the cooling agent, [151] a mixture of potassium nitrate, borax, and sodium or potassium chloride used in Super-rippite. A patent has also been taken out for the use of a fluoride or mixture of fluorides, more especially calcium fluoride or aluminium sodium fluoride, as a safety ingredient in blasting explosives. [152]

E. Lemaire [153] gives photographs of the flame produced at the moment of firing Colinite Antigrisoteuse, Explosifs A, B, C, D, and E, Dynamit Gomme, Yonckite No. 10, Alsilite, Permonite, and Antigel de Sûreté from a steel mortar and untamped into mixtures of coal dust and air and fire-damp in air, in a testing gallery. The charge limits found in this series of experiments are compared with those allowed by law. In a later paper [154] he gives a description of a safety blasting cartridge. With the object of reducing flame produced on firing blasting explosives in coal mines, and thus of minimising the chances of explosions of coal dust or firedamp air mixtures, the explosive cartridge is sur-

[148] Explosives, 1917, 1, 378 et seq.   [149] Explosives, 1919, 130.
[150] D. J. Metcalfe and others, Eng. Pat. 18138, 1914 ; J., 1915, 576.
[151] A. C. Pearcy, Eng. Pat. 7647, 1914 ; J., 1915, 101.
[152] Kynoch-Arklow and L. H. Pirmez, Eng. Pat. 110237 ; J., 1917, 1248.
[153] Ann. Mines de Belgique, 1914, 37.
[154] E. Lemaire, Ann. Mines de Belgique, 1914, 587.

rounded by a concentric layer of non-combustible material, consisting of a mixture of calcium fluoride and sodium chloride, or one of calcium fluoride, sodium chloride, ferrous sulphate, and fine sand. The layer is 5·0 mm. thick for dynamites and 3·5 mm. for S.G.P. explosives. The diminution in power caused by the use of this device is slight. The use of the safety cartridge renders possible a higher charge limit for safety explosives, and, to a great extent, converts dynamites into safety explosives.

PROPERTIES AND TESTING OF BLASTING EXPLOSIVES.

H. le Chatelier [155] gives a review in general terms of the various types of explosive in use at present. The power and rates of explo ion of these are discussed as well as the hygroscopicity, stability, fusibility, temperature of combustion, toxicity, etc.

A. Stettbacher [156] contributes a discussion of the limiting values of heat energy of decomposition of explosives. 1 kilo. of nitroglycerin yields 1580 calories; 1 kilo. of blasting gelatin 1620 calories; 1 kilo. of explosive consisting of 743 grms. of liquid air (95% oxygen) and 257 grms. of soot and crude naphthalene 2180 calories; 1 kilo. of ozobenzol, 2000 calories; 1 kilo. of glycerin trichlorate would yield 3000 calories and liquid hydrogen and liquid ozone 4500 calories. The energy of radioactive material is also discussed and possibilities of development in the direction of ozonides and oxozonides are indicated. Propylene oxozonide has already been prepared.

H. Muraour [157] gives a comparison of the values for the explosion temperatures of various mixtures of tolite and ammonium nitrate obtained in different ways. Values calculated on the basis of specific heats of Mallard and Le Chatelier or of Sarrau are higher than those calculated on the basis of the manometric table. Towards 1500° C. the former values approach those calculated from " C " pressure tables. The graph indicates that at high temperatures the temperatures from the manometric table will be above Mallard and Le Chatelier temperatures. In the interval 1500°–1700° C. temperatures calculated as above are below true temperatures. Temperatures calculated on the basis of Schreber's specific heats agree satisfactorily between 1300° and 2700° C. with those calculated from " C " pressure tables.

H. Kast [158] states that ordinary lead block tests taken alone cannot be used for a comparison of brisance of blasting explosives. The lead block test is applicable only when the explosives to be compared have similar detonation velocities.[159] Wilkinson [160] is under the impression

[155] *La Nature*, Feb. 20, 1915, p. 128.   [156] *Z. angew. Chem.*, 1917, **30**, 269.
[157] *Comptes rend.*, 1919, **169**, 723; *J.*, 1919, 927A
[158] *Z. ges. Schiess- u. Sprengstoffw.*, 1914, 33.
[159] *Sprengstoff, Waffen, u. Munit.*, 1914, 172.
[160] *J. Chem., Met., and Min. Soc. S. Afr.*, 1916, 409.

that experiments were made in Canada with enlarged lead blocks about twice as long as those used normally, and that results were considered better in every way than those obtained with the ordinary lead block, as indication of the practical utility of the explosive under examination.

A. von Huberth [161] describes an apparatus for measuring the brisance of an unconfined explosive charge. The explosive is fixed to the under side of a heavy steel plate which can be raised vertically between two guides. The motion of the plate is registered on a revolving drum.

J. A. Campbell [162] states that explosives containing notable amounts of aluminium, which have high temperatures of explosion, give abnormally high lead block results, probably owing to the erosion of the lead by the hot gases.

W. Nernst, [163] in a theoretical elucidation of the cause of oscillations observed with membrane manometers in determination of specific heats of gases by the explosion method, deduces a final equation which includes the cases of all measuring instruments provided with oscillating indicators in so far as it is a question of the relation of a reading to the true value of the magnitude. Slow pressure-rise curves which show oscillations do so first at half the pressure rise or later. The case of pressure rise and its registration was discussed also in connection with blasting explosives, the brisant and relatively slow types of which give characteristic curves.

J. J. Thomson [164] has applied the property possessed by tourmaline crystals of developing opposite electrifications at the two ends when subjected to compression along the axis, to the measurement of explosion pressures where the time during which the pressure exists is very small. The degree of electrification is proportional to the pressure applied. The method adopted is to electrify two parallel plates by means of a crystal under pressure and to shoot electrons in a vacuum tube between the plates. By this means it has been found that the maximum pressure developed in explosions of pure oxygen and hydrogen is attained in 1/16000 sec.

An account [165] is given of experiments carried out with mercury fulminate, picric acid, dynamite, cheddite, etc., at temperatures as low as −130° C. These lead to the following conclusions : (1) the sensibility of explosives to the action of mercury fulminate diminishes considerably at low temperatures, (2) the velocity of propagation of the wave of explosion varies with the amount below the freezing point, (3) the force of the explosion is not diminished by hard freezing, providing the detonator preserves its strength and assures complete explosion

[161] Z. ges. Schiess- u. Sprengstoffw., 1915, 281.
[162] J. Chem., Met., and Min. Soc. S. Afr., 1916, 66,
[163] Chem. Zentr., 1916, I., 868.
[164] Electrician, 1919, 463.   [165] Int. Military Digest, 1918, 548.

of the charge, and (4) at the freezing point of carbon dioxide the influence of cold is much diminished. Reasons for these phenomena* are put forward.

C. Herlin [166] gives an account of tests of explosives carried out in Sweden. Territ and Sternterrit ignite and burn without explosion when placed on a strongly burning fire in a sheet-iron enclosure. Flame from a fuse does not ignite them. Dynamites ordinarily used in Sweden, e.g., extra dynamite, express dynamite, and patent dynamite, do not pass this. test. A new sensitiveness test is described in which spheres of explosive weighing 50–100 grms. are allowed to fall upon an iron plate. By this test partially thawed blasting gelatin is less sensitive than frozen material and frozen gelatin dynamite is less sensitive than frozen blasting gelatin. Soft explosive could not be exploded at the heights used. Frozen blasting gelatin is less sensitive to initiation by a detonator than unfrozen.

C. Herlin [167] gives results of measurements of the velocities of detonation of several explosives in iron tubes (a) open at both ends, (b) closed at one end, (c) closed at both ends. The use of a tube closed at both ends is recommended for an international method for comparing velocities of detonation. From these results deductions are made as to the*usefulness of tamping in boreholes.

A. Aubert and S. A. G. Nauckhoff [168] patent the use of porous substances in blasting explosives in order to provide permanent air spaces whereby high velocity of detonation is maintained.

R. Forg,[169] in a paper on the "Measurement of the detonation velocity of modern explosives," gives tables and graphs showing the variation of velocity (1) with change in the diameter of the cartridge, the density being kept constant, and (2) with variation in density, the diameter being kept constant. The velocity increases with increase in the diameter of the cartridge and with increase in density; in some cases a maximum was reached followed by a considerable fall. The explosives investigated were picric acid, T.N.T., ammonal I, ammonal II, and* guncotton. The brisance and efficiency of an explosive cannot be deduced from the detonation velocity alone. The results obtained by Kast are given for comparison. The results of D'Autriche for variation in velocity with cubic density are given for Cheddit 60 bis, dynamite, and T.N.T.

* As the result of investigations on the D'Autriche test, H. Kast [170] concludes .that the use of a single length of detonating fuse on the lead base is preferable to that of two separate parallel tubes, the detona-

[166] *Z. ges. Schiess- u. Sprengstoffw.*, 1914, 390.
[167] *Z. ges. Schiess- u. Sprengstoffw.*, 1914, 236.
[168] Eng. Pat. 1283, 1915; *J.*, 1915, 1118.
[169] *Z. ges. Schiess- u. Sprengstoffw.*, 1916, 37.
[170] *Z. ges. Schiess- u. Sprengstoffw.*, 1919, 120.

tion waves proceeding in opposite directions from one extremity of the base to the other. Results are tabulated of detonation velocity tests by an improved Siemens spark chronograph, of T.N.T. detonating fuses of Belgian and German origin. In D'Autriche tests, sharp curvature of fuse must be avoided. A detonator for connecting fuse to explosive is only necessary when the latter is of low density and is lying free or is weakly tamped. No delay of transmission occurs at the fuse ends connected with the explosive. The D'Autriche method can never give very accurate results. Detonation velocities are given of T.N.T., trinitroanisol, amatol, and ammonal.

The theory of detonation is developed mathematically by R. Becker,[171] and from the equations deduced the following values are calculated (which are of the same order as the values experimentally determined). For a detonation temperature of 2000° C. in the case of nitroglycerin a detonation pressure 92,500 atmospheres is set up, and the detonation proceeds through the mass with a velocity of 7230 metres per sec.; for 2500° C. the corresponding figures are 110,500 atmospheres and 7930 metres per sec. For mercury fulminate, for detonation temperatures of 2000°, 2500°, and 3000° C., the detonation velocities calculated are 3690, 4120, and 4510 metres per sec., the pressures being 56,400, 70,400, and 84,500 atmospheres. These figures are of the same order as the values determined experimentally. The detonation temperature of mercury fulminate has been over-estimated.

M. Trautz [172] in the course of a paper on the velocity of chemical reactions, contributes a discussion of the velocity of detonation of explosives. The duration of a chemical process, i.e., of the molecular process which constitutes it, must be at least of the order of magnitude of the oscillation time. It is defined by heat of activation and equals 10^{-12} to 10^{-14} sec. In a column of a solid explosive 7 km. long initiated at one end, the series of 7×10^{-13} molecules will therefore react in 10^{-14} sec., i.e., the velocity of propagation is about 10 km. per sec., a value confirmed by practical measurement. The velocity of the explosion wave depends therefore on the heat of activation. That it advances more slowly in the case of gases in spite of the higher ignition temperature can only be explained on the ground that the radiation emitted from the place of ignition meets the other molecules under very small spatial angles.

According to C. Herlin,[173] frozen fresh extra dynamite propagates better than the soft freshly prepared explosive and propagation from frozen to soft is much better than the reverse. Similar relations hold for older explosive where propagation from soft to frozen fails even when cartridges touch. Properties of agridynamite, low freezing

[171] Z. Elektrochem., 1917, 23, 40; J., 1919, 879A.
[172] Z. anorg. Chem., 1919, 103, 154.
[173] Z. ges. Schiess- u. Sprengstoffw., 1914, 403.

territe, and sternterrite are described. The best position for initiating cartridges in boreholes is discussed. Difficulty of propagation of detonation along branches of detonating fuses when the coupled portions are so arranged as to require a sharp change in direction of the explosion wave is pointed out. No appreciable difference of detonation velocity was observed in the two halves of a cartridge 20 cm. long, in the middle of which the detonator was placed lengthwise.

A. Stettbacher [174] describes variations of explosive power with the method of initiation and shape of the explosive charge. The results obtained by means of primers and by cumulative initiation, *i.e.*, by the meeting of two explosion waves, are discussed. The higher the detonation velocity of the initiating material as compared with that of the explosive to be fired, the more efficient is this latter method of firing. Short-circuits may occur if this difference is too small, and the method then fails. Suggestions for arrangement of the fuse are made.

The application of Cordeau Bickford fuse or " Cordeau Detonant " in blasting is described by H. Souder. [175] Trials have shown that this fuse is safe and instantaneous and that it increases the efficiency of an explosive charge. The correct methods of joining separate portions of fuse to each other and to the detonator, and of connecting shot holes for simultaneous firing, are described and illustrated. Photographs and description of a blast by the Cornwall Ore Bank Co. are given.

Charges of insensitive dynamite [176] 40 in. in length were successfully detonated by inserting extra detonators without fuses at 5 in. intervals. In a 30 ft. charge a sharp explosion and great explosive force were obtained with electric detonators when one was placed 5 ft. from the top, one in the centre, and one 5 ft. from the bottom.

E. Maccullough [177] gives a simple method for calculating the quantities of explosive required in blasting. The quantity of explosive in use in any circumstance is given by $Q = cv^3$, where Q = quantity of explosive, c = a constant (0·3–0·45 for black powder and 0·06–0·09 for dynamite and other nitroglycerin compounds), and v = length of the line of least resistance in feet. The material thrown out by a blast is conical in shape and is represented by $V = 1·05h^3$ where V = volume in cubic feet, and h = vertical height. For all practical purposes the height is equal to the depth of borehole when the angle of inclination is less than 45°.

Propulsive Explosives.

The events of the past 'five years have, as already stated, greatly curtailed the amount of information published regarding developments

[174] *Z. ges. Schiess- u. Sprengstoffw.*, 1915, 16.
[175] *Trans. Amer. Inst. Min. Eng.*, 1914, 2547.
[176] *J. Chem., Met., and Min. Soc. S. Afr.*, 1914, 417.
[177] *J. Western Soc. Eng.*, 1915, 135.

in propellant explosives of the military class. Most of the information given has partaken rather of the nature of academic discussions regarding the nature of erosion, the phenomena of muzzle flashes, etc. No new explosive substance has been introduced, the various Powers still employing, in the main, either powders of the nitroglycerin-nitrocellulose type or pure nitrocellulose powders.

The blockade by the Allies forced the Central Powers to seek material other than cotton for the manufacture of nitrocellulose. An improved process for the preparation of relatively pure cellulose from wood had been introduced in Norway, and a further development which rendered it possible to produce this cellulose in a form extremely suitable for nitration rendered the use of this material possible for the manufacture of nitrocellulose. Cellulose produced in this way was first used by the Central Powers as a surgical wadding for field dressing stations, but on investigation it was found that purification could be carried to such a degree that it was quite suitable for use as a raw material in the manufacture of explosives. It is satisfactory to record that in the early days of the war the suitability of this material had been fully investigated in this country and that we were prepared to make use of it should the necessity arise.

At the outbreak of war cordite and cordite M D. were the Service propulsives in use in this country, and in the manufacture of these explosives acetone was used as the gelatinising agent. Only a small proportion of our requirements of this solvent could be produced in this country and the great bulk of it had to be imported from abroad. This was exceedingly undesirable in times of war and steps had to be taken to develop an alternative method for the manufacture of a suitable propulsive powder.

The Research Department, Woolwich, put forward a suggested composition in which the insoluble guncotton used in cordite and cordite M.D. was replaced by nitrocellulose soluble in ether-alcohol. Such a composition could be gelatinised by means of ether-alcohol, and this solvent could be produced in this country in practically unlimited quantities. Messrs. Curtis's & Harvey carried out the initial manufacturing trials with this new composition and these were sufficiently promising to warrant the submission of the proposal to the manufacturers of propulsive explosives throughout the country. On more extended trials, however, certain difficulties of manufacture presented themselves. It was found, for example, that the pressed cords tended to cohere during the drying operations. A good deal of exudation of nitroglycerin occurred and the dried powder was apt to contain air bubbles. Owing to the selection by Nobel's Explosives Company of a special grade of nitrocotton prepared within narrow limits of nitrogen content and a modification of the process of drying, these difficulties were overcome to such an extent that manufacture

on the large scale could be undertaken This new cordite was known as cordite R.D.B. and its composition is as follows: Nitroglycerin 42%, nitrocellulose (containing 12–12·2% N) 52%, mineral jelly 6%. Cordite R.D.B. was designed to give the same ballistics as cordite M.D. and its behaviour during the war showed it to be in no way inferior to cordite M.D. in this respect. Its adoption by the British Government was therefore amply justified by the results obtained in its use.

With the enormous increase in the quantity of explosives manufactured in this country by the use of a volatile solvent, the recovery of such solvents became of greatly increased economical importance.

The plant originally erected at the Royal Gunpowder Factory, Waltham Abbey, for the application of the bisulphite process for the recovery of acetone was found sufficient to deal with the increased quantities to be handled, and when the Royal Naval Cordite Factory was erected at Holton Heath this process was adopted and a plant on lines very similar to that in use at Waltham Abbey was installed. In some of the private factories acetone was recovered in various forms of plant by absorption in water and recovery by distillation, but this process has usually given lower yields than the bisulphite process.

With the introduction of cordite R.D.B. the bisulphite process was, of course, no longer applicable and a great deal of experimental work was undertaken to select a suitable absorbent. For a time sulphuric acid gave fairly satisfactory results, but the use of such a corrosive liquid for this purpose led to serious practical difficulties. The discovery by A. Daniel and J. H. Bregeat [178] of the affinity of hydroxylated hydrocarbons such as cresol for ether, and the absorptive power of these substances for alcohol finally solved this problem. The cresol method of recovery was applied in connection with the manufacture of cordite R.D.B. at Gretna, H.M. Factory, Pembrey, and at Ardeer Factory, with exceedingly satisfactory results, the recovery of about 50% of the total solvent used being quite a normal figure.

In connection with this question of economy in solvent used, it is of interest to record an attack upon this problem from another point of view. Solutions of nitrocellulose in ether-alcohol are of high viscosity, but it was known that different nitrocelluloses, though of the same nitrogen content, produced different degrees of viscosity at uniform concentration, and it was thought that it might be possible to select conditions of manufacture which would result in the production of a cellulose having a low viscosity figure and therefore consuming less solvent in manufacture, but suitable for the production of cordite R.D.B. in other respects.

An investigation having this object in view was therefore undertaken

[178] Eng. Pat. 127309; J., 1919, 521 A.

by the department of the Ministry of Munitions under the Director of Propellant Supplies, the Research Department,. Woolwich, and Messrs. Nobel's Explosives Co. Ltd., in collaboration. The details of this work have not yet been made public, but it may be stated that the object in view was satisfactorily attained. It was definitely established that the viscosities of the nitrocelluloses are related to those of the raw cotton from which they are made, and these again are dependent on the treatment to which the cotton is subjected. It has been possible, in the light of this information, to devise a scheme for the purification of cotton cellulose so that, on nitration, a nitrocellulose of low viscosity is obtained. The introduction of this modified process has resulted in very considerable economy in the solvent used in the production of cordite R.D.B., and has materially assisted in facilitating the control of this manufacture.

The problem of the production of a nitroglycerin-nitrocellulose powder without the aid of a volatile solvent was first solved by the invention in this country of ballistite. Since then, however, this type of propellant has received more attention on the Continent than in Great Britain. The study of this class of propellant has now been resumed in this country, and our knowledge regarding the technique of its manufacture in a fully stabilised condition so considerably advanced [179] that its obvious advantages should render its adoption in the future a matter of high probability.

In this connection Messrs. Nobel's Explosives Co. Ltd. put forward proposals for the manufacture of a new explosive under the name Ardeer Cordite. This explosive is the outcome of many years' research on the principles underlying the stabilisation and gelatinisation of explosives of the nitric ester class and marks a departure from explosives of the cordite type in that no volatile gelatiniser is employed in its manufacture and the requisite stability is obtained by entirely new means. The non-explosive ingredients are mixed with the nitroglycerin which is then added to the wet nitrocotton, according to the process discovered by C. O. Lundholm and J. Sayers. [180] After the excess of water has been expressed the resulting paste is rolled on hot rolls, when gelatinisation gradually takes place as the water is evaporated. A second rolling operation completes the gelatinisation and the rolled sheet may either be cut into flake form or it may be pressed in the warm condition in jacketed cylinders into any form that may be desired. This process possesses many advantages over the methods employed in the manufacture of cordite, and the resulting explosive possesses the further advantage over cordite of greatly increased stability.

A variation of the ordinary type of nitroglycerin-nitrocellulose pro-

[179] F. L. Nathan, W. Rintoul, and F. Baker, Eng. Pats. 4940 and 4941, 1913 ; J., 1914, 712. *Arms and Explosives*, Oct., 1919, 127.
[180] Eng. Pat. 6448, 1892 ; J., 1893, 290.

pellants has been suggested by the Powerite Explosives Company,[181] who propose the introduction of 2% of calcium picrate.

A powder of the ballistite type containing an addition of 5–7% phenanthrene has been protected by G. Spica.[182] The characteristic of Spica's powder is a considerably enhanced stability over the ordinary ballistite type made without a moderant.

While powders of the nitroglycerin type have hitherto been used by the British Government for arms of all calibre and for certain guns by the continental powers, the continental practice has been chiefly, and the American practice entirely, in favour of the adoption of powders of the pure nitrocellulose class. The high degree of erosion produced by nitroglycerin powders and their liability to develop abnormal pressures have been recognised as serious drawbacks, but their high energy content, their great chemical stability, their freedom from hygroscopic tendencies, and their regular ballistics have been strong points in their favour, particularly when naval requirements are to be met.

The most important cause of erosion is undoubtedly the temperature of the gaseous products of combustion of any powder, and it is in this direction, namely, the lower temperature of the products of combustion, that the superiority of nitrocellulose powders lies. This superiority, especially in small arms, has led to the adoption by the British Government of nitrocellulose powder for the 0·303 Lee Enfield rifle.

The development in nitrocellulose powders during the war period has mostly been in the direction of evolving a satisfactory progressive type of powder for small arms, with the object of obtaining a better velocity for standard pressures than can be obtained from the non-progressive type. As an example of the progress in this direction the du Pont Powder No. 16 may be cited. This is a tubular nitrocellulose powder stabilised with diphenylamine and surface-moderated with dinitrotoluene. It differs from the pre-war German explosives of this nature in being prepared from nitrocelluloses possessing a much higher nitrogen content and by a clearness of the colloid, the moderating agent being also different. The method of surface-moderation employed in the case of the du Pont powders is the subject of a series of patents.[183] For an account of the development of this class of powder the excellent work of Major Townsend Whelan in *The American Rifle* [184] should be consulted.

A method of obtaining progressive combustion without the aid of a non-volatile surface-moderating agent has been devised.[185] It

[181] Eng. Pat. 16505, 1915; *J.*, 1916, 656.
[182] Eng. Pat. 14004, 1914; Fr. Pat. 473264; *J.*, 1915, 576.
[183] U.S. Pats. 1308343, 1308344, and 1308346; *J.*, 1919, 605A.
[184] Century Co., New York, 1918.
[185] W. Eberlein, U.S. Pat. 1098237; *J.*, 1914, 769.

consists in the partial drying of nitrocellulose grains which have been gelatinised by a solvent in the ordinary way until a certain progressive density has been obtained. The grain is then submitted to a steeping process in a medium which removes the residual volatile solvent. It has always been considered a necessity in the manufacture of nitrocellulose powder gelatinised by means of an ether-alcohol mixture that for effective gelatinisation the nitrocotton should be free from water; for this reason it has been the custom to stove dry the nitrocotton before incorporation or to dehydrate it by means of alcohol. D. S. Kondratieff and B. Edelhertz [186] claim to be able to effect gelatinisation of a nitrocellulose containing as much as 25-30% of water.

The possibility of the production of a nitrocellulose powder without the aid of a volatile solvent has received attention, but in this instance the problem is much more difficult than in the case of the corresponding nitroglycerin-nitrocellulose class. The difficulties in manufacturing a pressed powder of this type are obvious, while the amount of non-volatile gelatinising agent that has to be used to effect gelatinisation so lowers the energy content of the powder as to make it unsuitable for ballistic purposes. C. Claessen [187] has patented a nitrocellulose powder which is made by gelatinising approximately 70 parts of nitrocellulose with 30 parts of nitro-derivatives of benzene, toluene, or phenol at high pressures and with the aid of warm rolls.

W. Macnab and B. J. Flürscheim [188] have developed a propulsive explosive consisting essentially of either tetryl or tetranitraniline, which together with other ingredients, are caused to cohere by the addition of a non-explosive colloidal substance such as rubber or gelatin.

With regard to the general question of the stabilisation of nitrocellulose powders, diphenylamine still appears to be the most suitable substance. In this connection an interesting observation of Bradley [189] is that at a stage when the powder has reached active decomposition, diphenylamine has become nitrated chiefly to the tetra- and hexanitro stage. Consequently it is not possible to fix definitely the limit to which diphenylamine will conserve the life of the powder.

The possibility of reducing muzzle flash has repeatedly engaged the attention of explosives technologists, but it cannot as yet be stated definitely what circumstances or combination of circumstances favour its production. Some authorities attribute it to the after-combustion of gases at high temperature, while others associate it with the ejection of unconsumed grains. Most efforts have been directed towards the employment of cooling agents, as, for instance, in the older patent of R. Sohlmann,[190] who introduced lithium salts with this object. J.

[186] U.S. Pat. 1212770 ; J., 1917, 403.
[187] Eng. Pat. 24713, 1913 ; see J., 1915, 852.
[188] Eng. Pat. 24702, 1913 ; J., 1915, 848. U.S. Naval Inst. Proc., 1915.
[190] Swedish Pat. 34505.

Delpech [191] shows that by the addition of vaseline or heavy petroleum oil to Poudre B the flame produced in the 75 mm., 105 mm., 120 mm., and 150 mm. guns is entirely extinguished, while, by modifying the quickness and load, normal ballistics were obtained. Substances such as carbon, naphthalene, cellulose, etc., were tried, but did not prove so successful.

Gunpowder.

Very little has appeared during the period under review to indicate what changes have taken place either in the composition or method of manufacture of black powder. With regard to variation in composition, two patents assigned by F. Sparre to the du Pont Co. have appeared. In the first of these,[192] the ordinary method of coating by means of graphite is replaced by the use of about 0·2% of a pulverised metallic substance containing aluminium, the ignition of the powder being thereby improved and the rate of glazing increased. In the second of these patents,[193] a substitute black powder is made employing water-soluble substances like sulphides or polysulphides of alkaline-earths instead of the sulphur, the charcoal being replaced, if so desired, by a water-soluble sulphonate. Claims are made to increased safety in manufacture while at the same time retaining the merit of cheapness.

Two patents [194] have been taken out by the du Pont Company which deal with processes and machines for the granulation of black powder. The methods are broadly a combination of two principles involving the forming of a pasty mass into plugs by forced sieving and the subsequent drying and formation into spherical grains by rolling on a sloping heated surface until thoroughly dry : the apparatus thus provides a continuous method for the production of finished grains starting with the milled material.

Sporting Powders.

With regard to sporting powders, nothing in the way of development in composition or method of manufacture has been published during the period of war. Apparently manufacturers are still content to employ the old procedure. An extremely interesting historical account of the development of this class of powder appeared in a series of articles in *Arms and Explosives* during the year 1917.

With regard to the question of testing the pressures developed in gun barrels by means of lead crushers, the long and arduous work which gave rise to the Field pressure table of 1913 has been brought to a fitting climax by the work carried out on behalf of Messrs. Eley Bros.

[191] *Comptes rend.*, 1919, 169, 537 ; *J.*, 1919, 878A.
[192] U.S. Pat. 1116944 ; *J.*, 1914, 1227.
[193] U.S Pat. 1128680 ; *J.*, 1915, 378.
[194] U.S. Pats. 1106087 and 1106138 ; *J.*, 1914, 943.

by Mr. H. ·W. R. Mason.[195] While the Field pressure table of 1913 gives values for all pressures in true proportion, actual absolute values were unknown. The factor for transforming the arbitrary value into true value has now been determined and we know that what was represented as a pressure of 3 tons on the Field table of 1913 is an absolute pressure of 2·55 tons. The work of Mason has standardised the table up to pressures of 10 tons, thus allowing of its application even to automatic pistols. Previous to Mason's work the idea was prevalent that in certain respects lead crushers gave anomalous results ; with the discovery of the spontaneous annealing of lead, these anomalies have been explained, so that lead crushers may now be standardised by the falling weight method. The true values for pressure derived from decrements appear in the Eley Standard Table of Pressures for 1918.

Initiating Explosives

From the time of the introduction of dynamite until about four years before the war, mercury fulminate was practically the only explosive used as an initiator of detonation. During the period immediately preceding the war various proposals were put forward according to which a portion of the fulminate charge of the detonator was replaced by another explosive, such as T.N.T., tetranitraniline, or tetryl. Such detonators have come to be known as composite detonators and the types which are most largely used are fulminate-tetryl and fulminate-T.N.T. detonators. In both these types mercury fulminate is still retained as the primary initiating agent.

About the year 1910 the Germans introduced lead azide as a substitute for mercury fulminate and predicted a great future for this new explosive. At least one firm equipped a large plant for the production of lead azide detonators on a commercial scale. Considerable quantities of these were produced, but in the spring and summer of 1914 doubt began to be thrown on the keeping properties of the azide, with the result that its progress as a substitute for fulminate received a severe check. The great demand that arose in 1915 for high explosive shell created a demand for a satisfactory detonator for these shells, and although loth to do so, the British Government were forced to adopt a mercury fulminate detonator.. The other belligerents used mercury fulminate as their primary initiating agent for high explosive shell, and in addition the Germans also used lead azide to some extent. Mercury fulminate still holds its position as the most important initiating explosive, and the developments which took place during the war were concerned more with the design of detonators for particular purposes than with the introduction of new detonating explosives.

[195] *Arms and Explosives*, 1918, 5 and 25.

The one objection to the use of mercury fulminate is the fact that on the absorption of a certain amount of moisture its ignition becomes difficult, and misfires occur.

C. Claessen [196] proposes to protect the charge of fulminate from moisture by covering it with a readily penetrable cap tipped by a stable detonating composition.

M. W. Quiggle and G. E. Bailey [197] propose the use of layers of nitro-cotton treated with camphor, which must be burned through before the detonators become ignited.

Little, if anything, appears to have been done of late years to improve the method of manufacture of fulminate or to effect economies of material. The nature of the by-products obtained in the process is reviewed at length by A. Langhans in a series of articles. [198] The author describes a deposit found in the condensing pipes of a fulminate plant. This is described as a double salt of mercurous nitrate and mercuric nitrate. Unlike other deposits which have been found in pipe connections from time to time, this compound is, of course, not explosive.

A comprehensive survey of work done on mercury fulminate, chiefly from an analytical point of view, has been given by G. S. Heaven. [199] According to the author, small crystals are more sensitive than large ones to friction tests under certain conditions, though he observes that large crystals are more sensitive to impact.

W. R. Hodgkinson, commenting on the above articles, [200] suggests that since nitrous acid is necessary to the formation of fulminate its action on alcohol may be expressed by the equation :

$$
\begin{array}{ccccc}
CH_3 & & & CH = N & \\
| & & & | & \\
CH_2 & + & N_2O_3 \rightarrow & \quad O & + \quad 2H_2O \\
| & & & | & \\
OH & & & C - N & \\
& & & | & \\
& & & OH &
\end{array}
$$
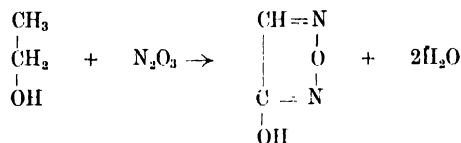
and that this " fulminic " acid immediately separates out as insoluble fulminate.

Various fulminates of other metals have been reported on from time to time, but so far none of them is likely to replace the mercury compound. The only fulminates which have been prepared by the interaction of nitric acid with the metal and then with alcohol are those of mercury and silver. The method of preparing anhydrous sodium fulminate by the action of sodium amalgam on mercury fulminate in

[196] Fr. Pat. 472540, 1914.   [197] U.S. Pat. 1088488.
[198] Z. ges. Schiess- u. Sprengstoffw., 1918, 345, 389, 406; 1919, 300, 318, 334, 350, 366; see J., 1919, 442A.   [199] J., 1918, 143T.   [200] J., 1918, 190T.

• presence of dry methyl or ethyl alcohol has been extended by L. Wohler and F. Martin [201] to the fulminates of cadmium, thallium and copper, the properties of which are described. Cadmium fulminate, $Cd(CNO)_2$, is soluble in the alcohols and water, its solution in the latter being decomposed by carbon dioxide with the liberation of the readily polymerisable fulminic acid. Its heat of decomposition is 170 calories per gram and its high calorific value, together with its high density, indicated that this salt would possess a powerful brisance. This was actually observed. In its sensitiveness to temperature rise and shock it approximates to mercury fulminate. Thallium fulminate, $TlCNO$, gives 223 calories per gram on decomposition. It is more sensitive to shock and rise of temperature than any other fulminate known. Cuprous fulminate, $CuCNO$, is hydrolysable with difficulty and may be prepared by the amalgam method under water. The dried substance has a grey colour with a greenish tinge. It has a calorific value of 508 calories per gram and is as sensitive to heat as the mercury and cadmium salts, but less sensitive to shock. Its density is less than that of other fulminates of heavy metals, but its brisance approaches that of cadmium fulminate.

The hygroscopic properties of potassium chlorate in admixture with mercury fulminate have been studied by G. B. Taylor and W. C. Cope.[202] They show that the rate of absorption of moisture by detonators containing these compositions is very nearly proportional to the differences in the vapour pressures between pure water and a saturated solution of potassium chlorate at the temperatures concerned. According to these authors fulminate-chlorate compositions do not absorb atmospheric moisture at all between 0° C. and 35° C., unless the air is at least 97% saturated, a condition only obtained in practice under very bad storage conditions.

As to the comparative efficacy of straight fulminate and of fulminate chlorate mixture, it has been pointed out that, although the detonation of fulminate mixture liberates 213 calories per gram-molecule as compared with 116 in the case of straight fulminate, the brisance of the former is nevertheless not so great as that of pure fulminate and the addition of oxidising materials in amounts calculated to secure complete combustion diminishes the velocity of detonation.[203]

G. B. Taylor and W. C. Cope [204] describe experiments with mixtures of fulminate and various oxyhalogen salts. With composite detonators containing T.N.T. or tetryl and a minimum charge of initiating mixture, it was found that all the 10% and 20% mixtures, with the possible

[201] Ber., 1917, 50, 586 ; J., 1917, 669.
[202] Met. and Chem. Eng., 1916, 15, 142 ; J., 1916, 944.
[203] A. Stettbacher, Z. ges. Schiess- u. Sprengstoffw., 1914, 341.
[204] U.S. Bureau of Mines, Tech. Paper 162, 1917 ; J., 1918, 672A.

exception of that containing potassium iodate, were more effective than pure fulminates.

Nitrates of silver and lead also gave more efficient mixtures than those of alkalis and alkaline-earths. Various oxides, such as manganese dioxide, cupric and ferric oxide, gave compositions less efficient than pure fulminate.

As a priming agent lead azide would have many advantages over mercury fulminate. That azide has not yet displaced fulminate is to be attributed to its occasional instability under apparently safe conditions. Suggestions for its stabilisation are therefore of interest. The Société d'Etudes Chimiques pour l'Industrie [205] propose to soak paper or other porous material in a solution of sodium azide and, after drying, to dip in a solution of lead acetate. It is claimed that the impregnated material may be cut with scissors without danger, provided a certain charge be not exceeded. It is generally assumed that the most important, if not the only factor rendering lead azide so unstable, is the size of the crystals. Crystals 3 mm. in length have been known to explode when brushed with a feather.[206]

In general, the azides require a much higher temperature to bring about their detonation than do the fulminates. In his pamphlet [207] F. Martin gives the following as the ignition temperatures of various fulminates and azides as obtained by the apparatus of L. Wöhler and O. Matter [208]: Silver azide $297°$, lead azide $327·5°$, mercurous azide $281°$, cadmium azide $291°$, cuprous azide $174°$, silver fulminate $170°$, mercury fulminate $186°$, cadmium fulminate $210°$, sodium fulminate $215°$ C.

Comparative sensitiveness tests quoted by Stettbacher [209] show lead azide to be much less sensitive than mercury fulminate to the shock of the fall hammer and of about the same sensitiveness as $80 : 20$ fulminate-chlorate composition.

That azide withstands high pressures without becoming "dead pressed" is well known. A. Stettbacher [210] discusses the effect of pressure on fulminate, fulminate-chlorate, and lead azide in detonators. When the pressures have been increased from 200 kilos. per square centimetre to 2000 kilos. the lead plates begin to show bad serrations both with pure fulminate and with $80 : 20$ composition. At 5000 kilos. pure fulminate becomes dead pressed, while chlorate composition misfires or gives weak plates, the falling off becoming even more marked at 10,000 kilos. On the other hand, with increased pressure lead azide improves rather than otherwise.

The azides of cobalt, nickel, manganese, and calcium have been

[205] Eng. Pat. 130166 , J., 1919, 742A.   [206] Sci. Amer. Suppl., Sept. 28, 1918.
[207] "Ueber Azide und Fulminate," published by A. Koch, Darmstadt, 1913.
[208] Z. ges. Schiess- u. Sprengstoffw., 1907, 2, 204.   [209] Ibid., 1914, 383.
[210] Loc. cit., p. 392.

prepared bʏ L. Wöhler and F.'Martin [211] by the action of an ethereal solution of hydrazoic acid on the suspended carbonate or basic azide. Attempts to prepare pure ferric and chromic azides were not successful. Both nickel and cobalt azides, which were obtained in the pure state, are particularly sensitive to friction, and the greatest caution must be exercised in handling them Zinc and manganese azides are both hygroscopic and readily hydrolysable.

, New methods for preparing azides have been patented by W. R. Hodgkinson.[212] In the first of these the azide is prepared by diazotising hydrazine sulphate in a solution maintained at as weak an acidity as possible. In the second of these patents, silver azide, which can be advantageously prepared according to the method described in the first patent, is washed with a solution of brine, whereby double decomposition into "insoluble silver chloride and soluble sodium azide takes place."

C. Claessen has proposed [213] to use simultaneously mercury fulminate and lead azide in compound detonators, the fulminate or its chlorate mixture being superposed above the azide, the main charge being tetryl or T.N.T. It is claimed that such a charge would be wholly insensitive to moisture. In a later patent,[214] the inventor replaces the fulminate by black powder, guncotton, smokeless powder, picrates, or perchlorates, the idea being that these substances would act as flame transmitters and ensure the detonation of the azide.

On the other hand, L. Wohler [215] uses lead azide as a priming for fulminate, claiming a greatly increased detonating effect thereby. He also asserts that fulminate, mixed with one-third its weight of azide, does not become " dead pressed." Mixtures of azide with diazobenzene nitrate or nitrogen sulphide are also claimed. W. Runge [216] mixes 70 to 95 parts of lead azide with from 30 to 5 parts of T.N.T. W. H. Buell [217] proposes a mixture of a suitable detonating azide and a nitrated body such as nitrocellulose as a priming charge in rim fire cartridges, a salt such as potassium carbonate, barium nitrate, or potassium nitrate being added.

Other alternatives to mercury fulminate besides lead azide are the diazo-perchlorates and lead styphnate, the salt of trinitroresorcinol, both proposed by E. R. von Herz.[218] The diazo-perchlorates possess the same high initiating power as lead azide, but unfortunately they show the same defect, in that explosion may occur without any appar-

[211] *Ber.*, 1917, **50**, 592 ; *J.*, 1917, 669.
[212] Eng. Pats. 128014 and 129152 ; *J.*, 1919, 604A, 698A.
[213] Eng. Pat. 13086, 1913 ; Fr. Pat. 459979 ; *J.*, 1913, 1171.
[214] Eng. Pat. 16456, 1913 ; *J.*, 1914, 845.
[215] U.S. Pat. 1128394 ; see *J.*, 1915, 378.
[216] U.S. Pat. 1168746 ; *J.*, 1916, 323.
[217] Eng. Pat. 21082, 1914 ; U.S. Pat. 1106343 ; *J.*, 1914, 944.
[218] Eng. Pat. 17961, 1914 ; Ger. Pat. 285902 ; *J.*, 1915, 1169.

ently adequate cause. An instance is on record of a quantity of *m*-nitrodiazobenzene perchlorate detonating while being carefully poured from a watchglass on to a sheet of glazed paper with a fall of less than 1 inch. Lead styphnate, on the other hand, is too low in initiating power to be used in this connection.

An interesting suggestion for the preparation of compounds of the diazo-class is that of F. Howles,[219] who obtains such substances as dinitrophenol diazo-nitrate by reducing picric acid to picramic acid with hydrogen sulphide and diazotising the product, thus :

$$C_6H_2(OH)(NO_2)— \rightarrow C_6H_2(OH)(NO_2)_2(NH_2) — \rightarrow C_6H_2(OH)(NO_2)_2N:N.NO_3.$$
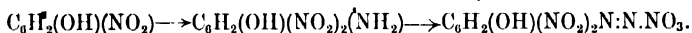
C. F. von Girsewald [220] claims that hexamethylenetriperoxide-diamine may be used as a prime explosive in T.N.T. detonators. 1 grm. of T.N.T. in a No. 8 detonator can be fired by 0·05–0·1 grm. of this substance with or without the aid of a reinforcing cap.

Sprengstoff A.-G. Carbonit [221] have taken out patents for 2.4.6.2′.4′.6′-hexanitrodiphenyl and hexanitrodiphenyl sulphide, both of which can be used in detonators. The former is obtained by the action of copper on chlorotrinitrobenzene in boiling toluene.

Trinitrophenylmethylnitramine, or tetryl, is still to be regarded as the most suitable substance for the secondary charge in composite detonators. There is but little recent comment on it in the literature, the most interesting paper being probably one by A. Stettbacher [222] on the tetryl "detonators" obtained by pressing the substance at 5000–6000 kilos. per sq. cm. These charges have specific gravity 1·78–1·80, and their weight varies from 10 to 50 grms., though with large charges it may even be expressed in kilograms.

Hexanitrodiphenylamine has been described as only slightly inferior to tetryl,[223] but its preparation from diphenylamine in one operation appears to be a dangerous process. The properties of its various salts have been studied by H. Kast and A. Langhans.[224]

Tetranitraniline is described by Lt. Bradley, U.S. Navy,[225] as the strongest explosive compound known. Its brisance is 1·5 times that of T.N.T. and it is more sensitive to shock. The Verona Chemical Company [226] describe it as being less sensitive than tetryl or picric acid and as giving a better lead block test. They propose its use instead of tetryl in compressed detonators.

Hexanitroethane is free from the objections offered to tetranitro-

[219] Eng. Pat. 125600; *J.*, 1019, 443A.   [220] Ger. Pat. 274522.

[221] Ger. Pat. 269826 and Eng. Pat. 18333, 1914; *J.*, 1915, 985. Eng. Pat. 18354, 1913; Fr. Pat. 460571; *J.*, 1914, 44.

[222] *Z. ges. Schiess- u. Sprengstoffw.*, 1919, 6; *J.*, 1919, 879A.

[223] *ibid.*, 1919, 89.

[224] *ibid.*, 1918, 1; *J.*, 1919, 927A.

[225] *Proc. Naval Inst.*, 1916, March–April; *Internat. Military Digest*, 1916, 430.

[226] *Chem. Abs.*, 1915, 139.

methane of being liquid and volatile, and it is proposed as a main charge for detonators alone or mixed with T.N.T.[247] According to W. Will,[228] however, hexanitroethane is unstable at slightly elevated temperatures.

J. B. Semple [229] suggests a salving of fulminate in an improved tetryl detonator by superposing silver acetylide to initiate the fulminate. Silver acetylide is described at length by Stettbacher.[230] The complex products obtained by passing acetylene into neutral or acid silver nitrate solution appear more promising than the simple acetylide, Ag_2C_2, obtained from an alkaline solution. They are more sensitive to heat than azides and show four times the initiating power of mercury fulminate.

F. L. Florens [231] describes some readily explosive double compounds of copper acetylide and cuprous sulphite, obtained by passing acetylene through a solution of copper sulphate and sodium bisulphite, but apparently no technical application is suggested.

Tetranitropentaerythritol, $C(CH_2NO_3)_4$, appears in the patent literature as a filling for detonation fuses, either alone or mixed with T.N.T.[232]

Objection has been taken to fulminate-chlorate compositions being used in caps owing to the fact that halogen introduces rust in gun barrels. Thus O. Mertens [233] suggests the use of a composition of mercury fulminate, barium nitrate, a basic substance such as carbonate or diphenylamine, with sulphide and phosphide of antimony. In an article to the like effect Utescher [234] states the cause of the rust to be the potassium chlorate and suggests such alternatives as barium nitrate, antimony sulphide, and the chromates of lead and mercury.

P. Medinger [235] attributes the rust to the action of mercuric chloride formed by the interaction of mercuric fulminate and potassium chloride. Potassium brontate has been proposed as an alternative to chlorate.[236] The inventor claims a higher detonating force for a 70:30 bromate mixture than for an 80:20 chlorate one. On the other hand, numerous misfires which occurred with primers containing potassium chlorate have been attributed by H. C. Pritham [237] of the Frankford Arsenal to the presence of potassium bromate.

E. Herz [238] describes the preparation and properties of the double

[227] C. Claessen, Fr. Pat. 463714; Eng. Pat. 24839, 1913; J., 1914, 576.
[228] Ber., 1914, 47, 965; J., 1914, 441.
[229] Eng. Pat. 133393; J., 1919, 927A.
[230] Z. ges. Schiess- u. Sprengstoffw., 1916, 1; J., 1919, 305A.
[231] Anal. Fis. Quim., 1913, 11, 320.   [232] J. Harle, Eng. Pat. 15355, 1914.
[233] Z. ges. Schiess- u. Sprengstoffw., 1914, 9, 70; J., 1914, 278.
[234] ibid., 1914, 104.
[235] Schiess und Waffen, 1915, 25.
[236] W. L. Main, U.S. Pat. 1147958; J., 1915, 924.
[237] J. Ind. Eng. Chem., 1917, 9, 990.
[238] Z. ges. Schiess- u. Sprengstoffw., 1916, Engineering, 1919, 348.

nitrate and hypophosphite of lead,' $Pb(NO_3)_2,Pb(H_2PO_2)_2$. It is recommended preferably for use in percussion fuses as being both sensitive and stable and giving a very hot flame.

Nitrogen sulphide, N_4S_4, is an important ingredient in cap compositions. C. Claessen [239] proposes its admixture with potassium chlorate or barium nitrate. The Rheinische Westfälische Sprengstoff A.-G. have a similar patent. The Deutsche Waffen- und Munitionsfabriken of Carlsruhe [240] have patented a priming cap containing red phosphorus. A suitable varnish is painted on the covering foil to separate the phosphorus from the mixture of chlorate and antimony sulphide which make up the charge.

A number of papers have appeared in recent years on the analysis of cap and detonator compositions. M. S. Losanitsch [241] determines mercury in fulminate by decomposing the latter with free acid and electrolysing. G. S. Heaven [242] finds the fulminate value with thiosulphate, a process which he discusses at length. The solution containing the mercury compounds is boiled with ferrous sulphate. Mercury is precipitated and weighed as sulphide, and the reduced chlorate obtained by titration with silver nitrate and ammonium thiocyanate. P. Nicolardot and J. Boudet [243] determine free mercury in fulminate by dissolving the fulminate in ammonium thiosulphate.

M. Marqueyrol and P. Loriette [244] separate cap composition ingredients with solvents. Nitro-compounds are removed by ether, chlorates and nitrates by water, and fulminate by potassium cyanide. The residue, presumably lead nitride, is boiled with acetic acid and any hydrazoic acid liberated distilled into silver nitrate and determined gravimetrically as silver azide.

A. Langhans [245] gives as a characteristic reaction of mercury fulminate the violet colour obtained by successively treating it with phenylhydrazine and dilute sulphuric acid. Langhans [246] has also shown that when mercury fulminate is heated with hypohalogenites or halogenates and hydrochloric acid, a blue oil is obtained, apparently the halogen-nitrosomethane, e.g., $CH_2Br.NO$. The same author [247] gives the results of experiments on the quantitative determination of fulminate. The methods include the decomposition of mercury fulminate with hydrochloric acid and estimation of the hydroxylamine with various standard solutions.

[239] Eng. Pat. 6057, 1913; Fr. Pat. 455369; J., 1914, 335.
[240] Ger. Pat. 274000; J., 1914, 769.
[241] Monatsh., 1914, 35, 307; J., 1914, 519.   [242] J., 1918, 145T.
[243] Ann. Chim. Analyt., 1918, 23, 206; J., 1918, 718A.
[244] Ann. Chim. Analyt., 1919, 114.
[245] Z. angew. Chem., 1918, 31, 161; J., 1918, 637A.
[246] J. prakt. Chem., 1918, 255.
[247] Z. anal. Chem., 1918, 57, 401; J., 1919, 389A

The sand test for detonators, originally proposed by W. O. Snelling in 1910, has been investigated by C. G. Storm and W. C. Cope.[248] The method, which consists in the measurement of the quantity of coarse sand pulverised by the detonation, has not yet been adopted in this country, though it is apparently accepted in America. G. B. Taylor and W. G. Cope [249] have shown that the quantity of sand crushed bears no relation to the priming efficiencies of various compositions, but that if detonators loaded with the same composition are considered, it is an accurate index of their relative efficiencies.

In a series of articles by A. Langhans [250] the author describes the appearance and marking of the lead plates, and contrasts them with those obtained on brass.

Acknowledgment is made of the valuable assistance rendered by various members of the Technical Staff of Messrs. Nobel's Explosives Co. in the preparation of this section of the report.

[248] *U.S. Bureau of Mines, Tech. Paper* 125; *J.*, 1916, 1132.
[249] *U.S. Bureau of Mines, Tech. Paper* 162; *J.*, 1918, 672A.
[250] *Z. ges. Schiess- u. Sprengstoffw.*, 1918, 97, 208, 227, 328.
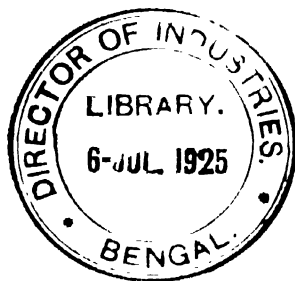
ANALYTICAL CHEMISTRY.

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In writing a report on the progress of analytical chemistry during the past year it has been necessary to take into consideration the fact that certain branches of the subject are dealt with at some length in the Annual Reports of the Chemical Society. To prevent overlapping, therefore, the rule adopted for abstracts in the Journals of the two Societies has been followed here, and prominence has accordingly been given to those subjects which are primarily of industrial importance.

A further difficulty has been that some of these technical analytical processes are more suitably discussed under special group headings, so that there was again a possibility of the duplication of the material. Where this seemed probable, the plan adopted in consultation with the writers of those reports has been to deal with matters of general analytical interest in this report, leaving those of more specialised interest to be discussed under the respective group headings. In other cases, where analytical matter has not been included to any great extent in a sectional report, it has been treated more fully in this report.

With regard to the arrangement of this report, an outline is first given of some of the principal forms of apparatus devised during the year, and of the application of various physical methods, and the other methods are then dealt with in the order adopted in the Journal.

APPARATUS AND PHYSICAL METHODS.

A useful portable cubic-foot standard for gas is described in an official publication of the U.S. Bureau of Standards.[1] It consists essentially of a cylindrical metal bell which can be moved up or down in an annular space in a tank containing oil to act as a seal for the gas. The innermost cylinder of the tank is closed at the top, and means are provided for regulating the height to which the bell can rise in the tank. The apparatus, which is made of aluminium, may be calibrated to deliver any desired quantity of air or gas.

For determining the density of gases a pycnometer has been devised

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[1] M. H. Stillman, *Techn. Paper No.* 114, 1919; *J.*, 1919, 796A.

without taps.[2] It consists of a cylindrical vessel with tapering ends, each of which has a capillary opening closed by clips and rubber fittings secured by screws. The vessel is filled with clean dry mercury, the gas drawn into it from a gasholder, and the density calculated by means of the formula,

$$d = \left(\frac{g-p}{Vs} + 1\right)\frac{1 + 0.00367t}{1 + 0.00367t'}g,$$

where g represents the weight of the pycnometer + gas ; p represents the weight of the pycnometer + air ; t the temperature at the time of filling ; and t' the temperature at the time of weighing ; s is the density of the air in the vessel at t ; and d the relative density of the gas (air=1).

Since Chardonnet artificial silk absorbs moisture rapidly, with alteration in the length of its fibre, it is a suitable material for hygroscopic measurements, and it has been adopted for this purpose in a device for measuring small quantities of moisture in gases.[3]

In order to obviate the action of organic liquids on the lubricants used with glass taps, an apparatus without stopcocks has been constructed for the estimation of vapour densities.[4] Two capillary tubes are fused to the top of one of the barometer tubes, and are then bent downwards and have their lower ends dipping into mercury reservoirs. The liquid is drawn into the barometer tube by raising and lowering the mercury reservoir. The difference between the levels in the two barometer tubes is measured, the mercury trough then lowered, and the difference in levels again measured, this process being repeated until concordant results are obtained at the different levels. A compact apparatus is described [5] which is suitable for the automatic estimation of small amounts of oxygen in gases, and for testing the air in mines and benzol distillation works for combustible gases. The method used is based on the contraction of volume which takes place during the combustion of oxygen or other impurity by means of an intermittently-heated electric wire. • The apparatus, which is provided with an automatic electric contact and means for cooling the gas and measuring the contraction in volume, is capable of detecting from 0.1% of oxygen.

A process of preferential combustion of carbon monoxide to carbon dioxide in the presence of a catalyst composed of a mixture of iron and chromic oxides with a small quantity of ceria and thoria is carried out in an instrument designed for the estimation of carbon monoxide in hydrogen.[6] Between 200° and 300° C. the catalyst oxidises the

[2] K, Kling and L. Suchowiak, *Metan*, 1917, **1**, 37 ; *Chem. Zentr.*, 1919, **90**, [IV.], 437 ; *J.*, 1919, 879A.

[3] A. T. Crockatt and R. B. Forster, *J.*, 1919, 95T.

[4] A. Morton, *J.*, 1919, 263T.

[5] H. G. Greenwood and A. T. S. Zealley, *J.*, 1919, 87T.

[6] E. K. Rideal and H. S. Taylor, *Analyst*, 1919, **44**, 89 ; *J.*, 1919, 252A.

carbon monoxide, but not the hydrogen. The carbon dioxide leaving the oxidation chamber is absorbed by standard calcium hydroxide solution, and the amount of carbon monoxide is estimated from the electrical conductivity of the solution considered in connection with the velocity of the gas, and the strength and rate of flow of the solution.

Another apparatus [7] for estimating carbon monoxide in mixtures of gases is a modification of that devised by Winmill and Graham.[8] A measured volume of the gas, after removal of carbon dioxide, is passed over iodine pentoxide heated to between 90° and 150° C., the carbon dioxide formed in the oxidation is absorbed in potassium iodide solution, and the liberated iodine titrated. For use in "safety" pits the difficulty of heating the iodine pentoxide is obviated by the use of a vacuum-jacketed flask containing oil of high boiling point, whilst for "naked light" pits the iodine tube is heated by means of electricity in an air bath.

A new form of helical absorption vessel is recommended for the efficient absorption of carbon dioxide by potassium hydroxide.[9] The gas is forced through the opening in the interior of two concentric chambers, and then slowly bubbles through a spiral formed in the annular space between the cylinders.

In another apparatus intended for the absorption of carbon dioxide or other gases by means of solid substances, the essential feature, is a pump the cylinder of which between the extreme positions of the piston is of definite volume. Either end of this cylinder may be put in communication, as desired, with the gas supply, the absorption vessel, a manometer, and the outer air.[10]

A still-head for use as a scrubber in the distillation of ammonia consists of a bulb with a side tube connected with the condenser, and a lower tube, connected at one end with the flask, and terminating at its other end in a perforated bulb within the larger bulb. The water first condensed surrounds the perforated bulb, and acts as a scrubber for the subsequent vapours.[11]

The principle adopted in an apparatus for measuring the volume of gas produced in a chemical reaction is to bring the gas to constant volume and temperature in a special form of burette, the lower end of which is connected with a water manometer. By measuring the pressure the correct volume is then obtained with an error not exceeding 0.1%.[12]

A simple form of apparatus for estimating oxygen in the upper

[7] J. I. Graham, J., 1919, 10T.

[8] J. Chem. Soc., 1914, 105, 1996; J., 1914, 944.

[9] J. Friedrichs, Z. angew. Chem., 1919, 32, 129; J., 1919, 443A.

[10] H. Strache and K. Kling, Ger. Pat. 308005; J., 1919, 30A.

[11] B. S. Davisson, J. Ind. Eng. Chem., 1919, 11, 465; J., 1919, 443A.

[12] P. Nicolardot and M. H. Robert, Chim. et Ind., 1919, 2, 641; J., 1919, 661A.

atmosphere is also based upon pressure measurements by means of a barometer tube and micrometer screw. The air is deoxidised with phosphorus, and the difference in pressure before and after deoxidation is compared with that of normal air.[13]

The use of a small electrolytic generator is recommended as a substitute for Kipp's apparatus for the production of small quantities of hydrogen in the laboratory. Distilled water is decomposed in a small glass cell consisting of a filter flask with a glass tube passing through the cork, the anode being a strip of sheet lead, and the cathode a piece of foil thin enough to be inserted, tightly between the cork and the neck of the flask. By reversing the current oxygen containing ozone is obtained.[14]

The use of the hydrometer for determining the density of liquids gives at best only an approximately correct result. The instrument may be rendered more sensitive without unduly decreasing the diameter of the stem, by introducing a tube of smaller diameter open at each end so that it passes through the stem and the weighted bulb, thus enabling the liquid to rise within the tube to the level of the liquid in which the hydrometer is immersed.[15]

An important series of papers was published in the Journal on refractometry, and its application to certain special branches of technical analysis. In the first of these papers J. C. Philip[16] gives an outline of the principles underlying refractometry and of their adaptation to the various types of instruments. In the second paper F. Stanley[17] points out the defects in certain older instruments, and shows how they have been remedied in improved types of British refractometers. The optical defect which prevents liquids of higher refractive index than 1·52 being examined has been remedied by constructing the prism of flint glass of suitable density. To eliminate drawbacks caused by the swinging of the whole instrument the mirror has been lengthened and placed in a position to illuminate the whole of the scale. An account of the methods of testing each of the parts of the instrument is given by F. Twyman and F. Simeon,[18] and of the special applications of the method in the sugar industry,[19] in the estimation of proteins in antitoxin sera,[20] and for testing chlorhydrin in the course of manufacture.[21] In the latter case it is shown that the percentage of chlorhydrin in an aqueous distillate may be accurately estimated from the refractive index of that distillate. A special application of refractometry to technical purposes is its use in

[13] F. W. Aston, *Chem. Soc. Trans.*, 119, 115, 472 ; *J.*, 1919, 535A.
[14] L. D. Williams, *J.*, 1919, 355T.
[15] P. Stevenson, Eng. Pat. 120659 ; *J.*, 1919, 30A.
[16] *J.*, 1919, 139T.   [17] *J.*, 1919, 141T.   [18] *J.*, 1919, 142T.
[19] H. Main, *J.*, 1919, 143T.   [20] A. Homer, *J.*, 1919, 145T.
[21] A. E. Berry, *J.*, 1919, 145T.

determining the composition of gases in, e.g., the recovery plant of nitrocellulose works, testing the efficiency of ventilation in mines, etc.[22] The method adopted in a form of apparatus for this purpose is to cause two rays from a common source of light to interfere after passing respectively through a tube containing the gas under examination and another tube containing a standard gas. The displacement in the position of the observed interference fringes when both tubes contain the standard gas is proportional to the difference between the refractive indices of the two gases.

The refractometer may also be used for the accurate estimation of alcohol in mixtures of alcohol and water, but it is essential that the alcoholic strength should not exceed 40%, since between 50 and 100% the same refractive indices are obtained at two points on the curve.[23]

A novel form of spectrophotometer has been described,[24] the aperture of which is composed of four sector-shaped openings, arranged diagonally about the optical axis, with the result that there is correct utilisation of all parts of the circular beam of light, whatever effective size the aperture may be. This increases the accuracy of ultra-violet ray absorption spectroscopy.

Mention may also be made of a photometer of general applicability, which is particularly suitable for such purposes as the determination of the absorptive power of solids and liquids, examination of the properties of luminescent surfaces, photochemical measurements, and measurements of the intensity of light.[25]

The adaptation of X-ray photography to the identification of substances in a mixture is a new instance of the application of physical methods in analytical chemistry. A beam of monochromatic X-rays is transmitted through a glass tube containing the finely powdered substance, and the diffraction patterns photographed. In the case of mixtures, each constituent produces patterns distinguishable from those produced by the others.[26]

FUEL AND GAS.

The discordant results obtained by different analysts in estimating the ash in coal and coke have been attributed to variations in the method of powdering the sample, especially when this has been done in an iron mortar.[27] Experiments have shown, however, that no appreciable error is caused by pounding the coke in an iron mortar, and the error

[22] M. Ponchon, *Chim. et Ind.*, 1919, **2**, 1647, *J.*, 1919, 661A.
[23] O. Faust, *Z. anal. Chem.*, 1919, **58**, 145; *J.*, 1919, 651A.
[24] S. J. Lewis, *Chem. Soc. Trans.*, 1919, **115**, 312; *J.*, 1919, 515A.
[25] L. Bloch, *J. Gasbeleucht*, 1919, **62**, 355; *J.*, 1919, 660A.
[26] A. W. Hull, *J. Franklin Inst.*, 1919, **188**, 131; *J.*, 1919, 661A
[27] Hughes, *Gas World*, Feb. 1, 1919.

must rather be attributed to variations in the methods of sampling the material in bulk.[28] A rapid method of estimating the ash in coal or coke without risk of losing volatile salts is to ignite the substance in a current of oxygen at about 600° C. The estimation may be combined with a determination of the total carbon.[29]

A special form of bomb provided with a removable fusion cup, with a cover which is held in position by a screw cap, has been devised for determining sulphur in coal by oxidation with sodium peroxide. The combustion is complete within half a minute. The method is also applicable to the estimation of sulphur in pyrites and in rubber, and of halogens in organic compounds.[30] The Kjeldahl method is commonly used for the determination of nitrogen in coal and coke, but it has been shown that, as usually applied, it gives results which vary with conditions and are invariably lower than those obtained by the Dumas method or Simmerbach and Sommer's modification of that method.[31] A modification of the Kjeldahl method in which the oxidation was effected at a low temperature and a correction applied for the loss of nitrogen gave the same results as Dumas' method.[32]

The theory of probability has been applied to the estimation of the probable errors in the analysis of coal, and it has been calculated that on a 5 lb. gross sample the probable limits of error in sampling are 0.2%, for ash 0.4%, for moisture 0.2%, and for heating value 0.75%.[33]

The presence of bases such as pyridine and amines causes difficulties in the estimation of ammonia in the aqueous products of the distillation of shales, lignites, and coals. To obviate this a modification of the hypochlorite or hypobromite method, with a special form of apparatus, has been devised.[34] A convenient and accurate method of determining the total sulphur in coal gas is described. A measured quantity of the gas is burned in Drehschmidt's apparatus, and the products of the combustion aspirated through two flasks respectively containing equivalent quantities of iodine and thiosulphate solutions, and the excess of thiosulphate left after the combustion is titrated with standard iodine solution.[35]

Attention may also be directed to an experimental study of the method of determining benzol in coal gas by freezing.[36]

For the determination of tar vapour in producer gas a filter tube of

[28] A. E. Findley, J., 1919, 93T.
[29] W. Erhard, Chem.-Zeit., 1919, 43, 422 ; J., 1919, 614A.
[30] S. W. Parr, J. Ind Eng Chem., 1919, 11, 230 ; J., 1919, 242A.
[31] E. Terres and others, J. Gasbeleucht., 1919, 62, 173 ; J., 1919, 399A.
[32] J., 1916, 102.
[33] J. D. Davis and J. G. Fairchild, Bureau of Mines, Tech. Paper 171, 1918 ; J., 1919, 563A.
[34] P. Nicolardot and H. Baurier, Chim. et Ind., 1919, 2, 777 ; J., 1919, 708A.
[35] M. Hirsch, Chem.-Zeit., 1919, 43, 482 ; J., 1919, 707A.
[36] St. Claire Deville, Gas J., 1919, 147, 392 ; J., 1919, 672A.

special construction has been devised. It is packed with cotton wool and asbestos and, suspended in ice water.[37]

MINERAL OILS, ETC.

The mercurisation grade [38] indicates the progress of the refining of petrols and lamp oils. It also affords a test of the presence of unsaturated constituents which combine with mercuric acetate. The oil is boiled beneath a reflux condenser with an alcoholic solution of mercuric acetate and the unaltered hydrocarbons,,distilled in a current of steam. The combined hydrocarbons are then liberated with acid and also distilled.

A method of analysing petroleum spirit has been based on the determination of the critical temperature of solution in aniline of the sample before and after removal of aromatic hydrocarbons by nitration, and washing with sulphuric acid. From the results the amount of aromatic hydrocarbons can be calculated by means of a formula. The addition of benzene to a mixture of hydrocarbons free from aromatic hydrocarbons depresses the critical temperature of solution in proportion to the amount added, the ratio being 1:1·14. For toluene the ratio is 1:1·19, and for xylene 1:1·21.[39]

Results obtained by F. B. Thole [40] in regard to the determination of aromatic hydrocarbons in petrol have been confirmed, and his method extended to the calculation of the expansion which takes place on mixing aromatic hydrocarbons with petrol of definite sp. gr. A determination of the amount by which the observed sp. gr. was less than that found by calculation showed that in the case of toluene and xylene the expansion was practically the same, but was double in the case of benzene. Graphs have been constructed from which the correct deviation due to expansion can be directly read.[41]

The calorific value of petrol may be accurately determined by weighing it in a sealed glass bulb, which is then ignited, together with a small weighed quantity of naphthalene, in a calorimetric bomb. The heat of ignition of the naphthalene bursts the glass bulb, and there is no loss of petroleum spirit.[42]

A method of determining paraffin wax in mineral oils has been based on the fact that a hot solution of the oil in butanone (methylethyl ketone) yields a deposit of the pure wax on cooling. The precipitation is best carried out at about −15° C. from a solution in a mixture of butanone

[37] A. Zschimmer, *J. Gasbeleucht.*, 1919, **62**, 53 ; *J.*, 1919, 243A.

[38] J. Tausz and H. Wolf, *Z. angew. Chem.*, 1919, **32**, 317 ; *J.*, 1919, 889A.

[39] A. Chavanne and L. J. Simon, *Comptes rend.*, 1919, **169**, 70, 485 ; *J.*, 1919, 619A, 672A.

[40] *J.*, 1919, 39T.   [41] H. G. Colman and E. W. Yeoman, *J.*, 1919, 82T.

[42] A. Philip, *Analyst*, 1919, **44**, 95 ; *J.*, 1919, 244A.

with 1·3% of water. The test is applicable to the estimation of paraffin wax in candles.[43]

Holde's method of determining asphalt (*J.*, 1909, 831) is not trust-worthy when the oil contains paraffin wax. In such cases the wax must be separated from the asphalt, preferably by treatment with purified petroleum spirit.[44] Asphalt separated in this way, with the aid of centrifuging, can be purified by repeated solution in benzene, and reprecipitation with petroleum spirit. The results agree within about 0·2% of those obtained by Holde's method.[15]

TAR AND TAR PRODUCTS.

A comparative study of the various methods of estimating phenol in tar oils has shown that the methods of J. J. Fox and M. F. Barker,[46] and of J. M. Weiss and C. R. Downs [47] are the best, the former giving somewhat lower results than the latter, but having the advantage of speed. Removal of the water by drying over calcium chloride causes the results to be too high, whilst distillation without drying gives rather low results. Since no method is accurate within about 1%, no exception need be taken to a modification of Fox and Barker's method, in which the water is removed by distillation with benzol, and moisture is excluded in the subsequent processes.[48]

A method has been worked out for estimating benzene and toluene when mixed with petrol as a motor fuel.[49] The aromatic hydrocarbons are removed by sulphonation with strong sulphuric acid, and their amount is estimated by determining the specific gravity of the liquid before and after sulphonation. Since the specific gravity of a mixture of hydrocarbons is not the arithmetical mean of the specific gravities of its constituents it is necessary to apply a correction obtained by con-structing " deviation curves " from the results given by experimental mixtures.

The degree of purification of commercial benzol may be ascertained by the cryoscopic method. Pure benzene freezes at 5·48° C., and the cryoscopic constant for dilute solutions of toluene in benzene is 4·92. The percentage of benzene in a commercial sample may be calculated from the freezing point, t, of the liquid by the formula $x = 90·51 + 1·73t$ in the case of dry samples, and $x = 90·68 + 1·73t$ in the case of wet samples. The method gives more trustworthy results than other methods and has the advantage that the presence of paraffin hydro-carbons having the same boiling point as benzene is indicated by the

[43] F. Schwarz, *Mitt. k. Materialpruf.*, 1918, **36**, 241 ; *J.*, 1919, 453A.
[44] S. Prozynski, *Petroleum*, 1918, **14**, 9 ; *J.*, 1919, 213A.
[45] J. Tausz and A. Lüttgen, *Petroleum*, 1919, **14**, 653 ; *J.*, 1919, 754A.
[46] *J.*, 1918, 265T.
[47] *J. Ind. Eng. Chem.*, 1917, **9**, 569 ; *J.*, 1917, 863.
[48] J C. Petrie, *J.*, 1919, 132T.   [49] F. B. Thole, *J.*, 1919, 39T.

depression in the freezing point.[50]   In order to bring the freezing point
of a mixture to 0° –1° C. so as to be within the region in which the
freezing point is proportional to the amount of benzene a known weight
of pure benzene is added.   From the weights of pure benzene and crude
benzol and the respective freezing points of the two liquids the per-
centage of benzene in the original sample may be calculated.[51]   The
same method has been used for determining the degree of purity of
dimethylaniline,[52] and for estimating the nitrobenzene in commercial
nitrobenzols.[53]

A determination of the critical temperature of solution of a commercial
sample of toluene, benzene, or xylene in about 90% acetic acid affords
a means of estimating the amount of paraffin hydrocarbons present.
The solvent is standardised upon the pure aromatic hydrocarbon.   In
the case of toluene the presence of 1% of pentane raises the critical
temperature by 0·9° C., whilst octane raises it by 1·6° C.   Less than
1% of paraffin hydrocarbons may therefore be estimated by this
method in commercial toluene.[54]

Northall-Laurie's method [55] of determining toluene in commercial
toluols has been adapted to the determination of monochlorobenzene
in crude chlorinated benzene.[56]   The sample is distilled, the boiling
point of the first and last fractions, obtained under specified conditions,
is determined in special constant boiling-point flasks, and the com-
position of the sample is then found by reference to a graph con-
structed from the results of determinations made on mixtures of known
composition.

Another method of analysing mixtures of benzene, chlorobenzene,
and dichlorobenzene is based upon similar principles to a method
devised by Coman.[57]   The sample is distilled under uniform conditions
so as to obtain three samples boiling respectively up to 122° C., from
122° to 142° C., and above 142° C.   From the amounts of these frac-
tions the percentages of benzene and chlorobenzene are obtained by the
use of a graph embodying the results given by mixtures of known com-
position, whilst the dichlorobenzene is found by difference.   The
weights of the constituents are calculated from the specific gravities.[58]

A comparative study of different methods of estimating thiophen in
benzene has been made.[59]   A modification in which Denigès' reagent

[50] W. J. Jones, *J. Soc. Dyers and Col.*, 1919, **35**, 45 ; *J.*, 1919, 216A.
[51] W. J. Jones, *J.*, 1919, 128T.
[52] W. J. Jones, *J. Soc. Dyers and Col.*, 1919, **35**, 43 ; *J.*, 1919, 217A.
[53] C. Simpson and W. J. Jones, *J.*, 1919, 325T.
[54] K. J. P. Orton and D. C. Jones, *Chem. Soc. Trans.*, 1919, **115**, 1055 ; *J.*, 1919, 811A.   [55] *J.*, 1915, 950.
[56] N. G. S. Coppin and F. Holt, *Analyst*, 1919, **44**, 226 ; *J.*, 1919, 568A.
[57] *J. Gas Lighting*, 1915, **129**, 196 ; *J.*, 1915, 168 ; 1919, 57T.
[58] P. F. Frankland, S. R. Carter, and D. Webster, *J.*, 1919, 153T.
[59] P. E. Spielmann and S. P. Schotz, *J.*, 1919, 188T.

(basic mercuric sulphate solution) is shaken with the benzene gives good results, only the thiophen, and not the carbon bisulphide or other substances which accompany it, being precipitated. The precipitate is dried at 110°–115° C. and weighed. Trustworthy results are also obtained by the use of a modified form of Paolini and Silbermann's reagent (basic mercuric acetate), which combines with thiophen to form an insoluble compound, $SC_4(HgC_2H_3O_2)_4$. The precipitate is washed with cold water, dried at 110° C., and weighed. In testing commercial benzols for thiophen by means of the indophenine reaction it is advisable to add an oxidising agent, preferably a drop of nitric acid, to the sulphuric acid, since, as Bauer [60] pointed out, the blue coloration is not obtained when pure sulphuric acid is used.[61]

Of the various methods proposed for the estimation of carbon bisulphide in benzene, the change in the specific gravity of the liquid after removal of the carbon bisulphide enables about 0·03% of that substance to be estimated. Oxidation with bromine gives accurate results, but a large excess of potassium hydroxide, and subsequently of bromine, must be added, and sufficient time allowed for the oxidation. Titration of the xanthate solution with standard copper sulphate solution is unsatisfactory mainly owing to the effect of the large excess of acetic acid. A gravimetric method has been based on the reaction between copper sulphate and carbon bisulphide, cupric xanthate being first formed and then decomposed into cuprous xanthate and dixanthogen, but the cuprous xanthate is not obtained in a pure condition. Precipitation with phenylhydrazine is only useful as a qualitative test.[62]

A simple colorimetric method of estimating small quantities of aniline in aqueous solution has been based on the formation of Runge's Violet, by the action of sodium hydroxide and phenol, and comparison of the colour with that given by water containing definite amounts of aniline.[63]

For the separation of anthracene, carbazole, and phenanthrene from "anthracene oil" a scheme based on a treatment with naphtha has been devised. The carbazole may be rapidly estimated from a determination of the nitrogen by a modification of Kjeldahl's method, which gives results in close agreement with those obtained by the nitrometer method.[64]

COLOURING MATTERS AND DYES.

A method of titrating p-aminoazobenzene has been devised in which the substance is dissolved in alcohol and the solution acidified with hydrochloric acid and titrated with standard nitrite solution, iodide-starch paper being used as indicator.[65]

[60] Ber., 1904, 37, 3128. [61] E. Wray, J., 1919, 84T.
[62] P. E. Spielmann and F. B. Jones, J., 1919, 186T.
[63] W. G. O. Christiansen, J. Ind. Eng. Chem., 1919, 11, 763 ; J., 1919, 756A.
[64] J. M. Clark, J. Ind. Eng. Chem., 1919, 11, 204 , J., 1919, 247A.
[65] F. Neitzel, Chem.-Zeit., 1919, 43, 472 ; J., 1919, 712A.

ACIDS, ALKALIS, SALTS.

Nitrous and Sulphurous Acids.

The volumetric methods commonly employed for the estimation of nitrous acid and nitrites give inaccurate results. These errors are obviated in a method in which the nitrite solution is run into an excess of acidified standard permanganate solution, the excess of permanganate reduced with ferrous sulphate or other reducing agent, and the excess of the latter titrated with permanganate.[66] The presence of fluorides interferes with the oxidimetric determination of nitrous acid, by causing the oxidation to follow a different course, with the formation of Mn_2O_3 instead of MnO_2. This may be obviated by combining an iodometric method with the oxidimetric method. An excess of standard permanganate solution is added in the presence of sulphuric acid, then alkali iodide, and the liberated iodine is titrated.[67] Attention has also been drawn to various sources of error in the iodometric titration of sulphurous acid, such as oxidation by atmospheric oxygen, the effect of which is increased by the presence of sodium carbonate and hydrochloric acid. To obtain accurate results it is essential that the sulphurous acid solution should be run into the iodine solution.[68]

Cyanides.

It has been pointed out [69] that Feld's method of estimating cyanide in ammoniacal liquors gives low results if the liquid also contains free ammonia, and that the method of Colman and Yeoman [70] is untrustworthy in the presence of thiosulphates owing to the lead thiosulphate being decomposed during the distillation. These difficulties are obviated in a colorimetric method of estimation based on the conversion of ammonium cyanide into thiocyanate by treatment with ammonium polysulphide and colorimetric estimation of the thiocyanate as ferric thiocyanate.[71] The method has been extended so as to include thiocarbonates, which are converted into thiocyanate by digestion with ammonium polysulphide at 75° C. without affecting the cyanide, whilst the latter is converted into thiocyanate by digestion at 30°–35° C. without affecting the thiocarbonate.[72]

[66] J. S. Laird and T. C. Simpson, *J. Amer. Chem. Soc.*, 1919, 41, 524 ; *J.*, 1919, 359A.

[67] I. Bellucci, *Gazz. Chim. Ital.*, 1919, 49, I., 209 ; *J.*, 1919, 627A.

[68] I. M. Kolthoff, *Pharm. Weekblad*, 1919, 56, 1366 ; *J.*, 1919, 815A.

[69] 55th *Ann. Rep. on Alkali Works*; *J.*, 1919, 716A.

[70] *J.*, 1918, 322T.

[71] P. E. Spielmann and H. Wood, *J.*, 1919, 43T.

[72] P. E. Spielmann and H. Wood, *J.*, 1919, 369T.

Peroxides.

For the direct iodometric estimation of hydrogen peroxide a few drops of dilute ammonium molybdate solution are added, as a catalyst, after the addition of the potassium iodide and acid, and the liberated iodine immediately titrated.[73]

Iodometric methods of determining the active oxygen in sodium peroxide give low results, and the same remark applies to methods in which the peroxide is decomposed with water, and the liberated hydrogen peroxide titrated with permanganate solution. This is to be attributed to partial decomposition of the hydrogen peroxide by the manganese sulphate formed during the titration. It may be obviated by adding the sodium peroxide to a solution containing sulphuric acid and boric acid, and then titrating the liberated hydrogen peroxide. The older method in which the oxygen is liberated from the peroxide by water in the presence of cobalt nitrate gives too high results, but by substituting copper sulphate for cobalt nitrate as catalyst the method is rendered trustworthy.[71]

Lime.

It has been shown that the tables ordinarily employed for estimating the amount of calcium oxide in milk of lime from the specific gravity are inaccurate. A table based on the results obtained by the use of a pycnometer has been constructed to replace those based on hydrometer determinations.[75]

Ferrocyanides.

The behaviour of various ferrocyanides towards chlorine and bromine has been studied, and it has been shown that nickel and bismuth are precipitated quantitatively as ferrocyanides.[76]

METALS AND ORES.

Iron and Steel.

Several methods have been published in the course of the year for the complete analysis of various ores, alloys, etc., and some of these have included modifications which have increased the accuracy of the estimation of individual constituents, or have rendered the whole process more rapid. For example, a method of estimating magnetite in copper matte and slag has been based on the fact that ferric iron in the fresh matte and slags is present entirely in the form of magnetite, so that

[73] I. M. Kolthoff, *Pharm. Weekblad*, 1919, 56, 949; *J.*, 1919, 575A.
[74] J. Milbauer, *J. prakt. Chem.*, 1918, 98, 1; *J.*, 1919, 10A.
[75] G. Lenart, *Z. ver. deuts. Zuckerind.*, 1919, 1; *J.*, 1919, 533A.
[76] F. F. Werner, *Z. anal. Chem.*, 1919, 58, 23; *J.*, 1919, 461A.

the amount of magnetic oxide may be calculated from a determination of the ferric iron.[77]

The use of soda-asbestos as an absorbent for carbon dioxide [78] in the estimation of carbon in steel has the advantage that it is capable of absorbing about 10% of its weight of carbon dioxide while the gas is passing through it at a rapid rate. A special form of absorption vessel has been devised for the purpose.[79]

The principle embodied in an electrolytic method of determining carbon in steel is capable of application to other analytical processes. The carbon dioxide produced in the combustion is absorbed by a solution of barium hydroxide, and the change in the electrolytic resistance of this solution after precipitation of barium carbonate affords a means of estimating the carbon with an error of less than 0·005%. A table has been constructed showing the percentages of carbon corresponding to the resistance and temperatures of barium hydroxide solutions of definite concentrations.[80]

The conditions necessary for the rapid and accurate estimation of phosphorus as molybdate in steel containing vanadium have been determined. Contrary to the general opinion, the addition of too great an excess of ferrous sulphate to dissolve the manganese dioxide precipitate and reduce vanadic acid to the hypovanadic condition causes the results to be too low. In the case of steel containing vanadium more free ammonia is required than with ordinary steels; at least 66 times the theoretical amount of MoO_3 is necessary to precipitate the phosphorus, and the precipitation must be made below 20° C. to prevent simultaneous precipitation of vanadium.[81] In the usual methods of estimating phosphorus in steel, iron, etc., by the molybdate method the oxide MoO_2 is sometimes also precipitated. This may be prevented by rendering the solution strongly acid with nitric acid before the precipitation. The addition of an excess of the reagent and of ammonium nitrate causes the precipitation to be complete.[82] A method has also been devised for the direct estimation of phosphorus in iron and steel, without preliminary separation of arsenic.[83]

A process of selective oxidation with nitric acid has been used for the estimation of vanadium and chromium in steel, the conditions being such that the vanadium is oxidised while the chromium remains unoxidised. The liquid is then titrated electrometrically by means

[77] F. G. Hawley, *Eng. and Min. J.*, 1919, **108**, 308; *J.*, 1919, 725A.

[78] *J.*, 1916, 1237.

[79] L. J. Rogers, *Canadian Chem. J.*, 1919, **3**, 122; *J.*, 1919, 418A.

[80] J. R. Cain and L. G. Maxwell, *J. Ind. Eng. Chem.*, 1919, **11**, 852; *J.*, 1919, 773A.

[81] J. Maitchell, *Chem. News*, 1919, **119**, 212; *J.*, 1919, 906A.

[82] A. Travers, *Chim. et Ind.*, 1919, **2**, 133; *J.*, 1919, 256A.

[83] N. D. Ridsdale, *Proc. Cleveland Inst. Eng.*, 1919, 155; *J.*, 1919, 581A.

of the method and apparatus ,previously described,[84] and a correction is applied for the unoxidised vanadium (about 1%). · Both chromium and vanadium are then oxidised together in another portion of the solution, the liquid titrated,[85] and the amount of chromium obtained by difference.[86]

Titanium.

Titanium in iron ores may be estimated by fusing the sample with sodium peroxide, separating iron as sulphide, precipitating the titanium in the filtrate with "cupferron" (ammonium salt of nitrosophenyl-hydroxylamine), igniting the precipitate. and weighing the residue of TiO_2. Or the titanium in solution may be estimated colorimetrically by means of hydrogen peroxide.[87] A colorimetric method has also been used for the estimation of titanium in puzzuolanas. Titanium sulphate affords a suitable compound for the preparation of standard solutions, the amount of TiO_2 being determined by igniting the salt with successive quantities of ammonium carbonate and weighing the residue. The presence of ferric sulphate does not interfere with the colorimetric estimation.[88]

RARE METALS.

A method of separating platinum and iridium has been based'on the precipitation of the former as ammonium chloroplatinate, leaving the ammonium chloroiridate in solution.[89]

Zirconium.

In a scheme for the analysis of zirconium ores the material is fused with sodium peroxide, the bulk of the silica separated, and the zirconium and titanium precipitated together from nearly neutral solution by means of sodium thiosulphate. The precipitate is ignited and weighed, silica separated by treatment with sulphuric and hydrofluoric acids, titanium estimated colorimetrically, and the non-volatile residue (zirconia) deducted from the original weight.[90]

Uranium.

The presence of iron, aluminium, and vanadium, which are the impurities of most common occurrence in carnotite, interferes with the separation of uranium. This may be obviated by adding an excess of

[84] J., 1917, 1011.   [85] J., 1916, 966.

[86] G. L. Kelley, J. A. Wiley, R. T. Bohn, and W. C. Wright, J. Ind. Eng. Chem., 1919, 11, 632; J., 1919, 583A.

[87] J. Waddell, Analyst, 1919, 44, 307; J.,'1919, 775A.

[88] A. Cavazzi, Annali Chim. Appl., 1919, 12, 105; J., 1919, 580A.

[89] E. H. Archibald and J. W. Kern, Trans. Roy. Soc. Canada, 1917-1918/11, 7; J., 1919, 40A.

[90] A. Travers, Chim. et Ind.. 1919. 2. 385; J., 1919, 421A.

ferric iron to the solution, precipitating the iron, vanadium, and most of the aluminium with sodium carbonate at about 90° C., and then precipitating the uranium from the boiling filtrate by means of sodium hydroxide. After reprecipitation to separate the last traces of impurities, the precipitate is ignited, and the residue weighed as uranium oxide, U_3O_8.[91]

FATS, OILS, WAXES.

Apart from descriptions of the analytical characters of individual oils and fats, which are dealt with in the Report on the subject, there have not been many contributions to this branch of analytical chemistry. Among those of more general chemical interest the most important are those dealing with the determination of the acetyl value. Attention has been drawn to the fact that a slight hydrolysis may occur when the acetylated product is repeatedly boiled with water, and that as a safeguard the free acidity should be titrated in the cold before determining the saponification value of the acetylated oil.[92] The determination of the acetyl value either by the original method of Benedikt and Ulzer or by Lewkowitsch's modifications involves several possible errors. In the case of fatty acids, mixed anhydrides may be formed, which cause the results to be too high, or inner esters of hydroxy-fatty acids may be produced. In the case of neutral fats, reciprocal esterification with the acetic anhydride may occur, and it is difficult to distinguish between the different kinds of hydroxylated compounds. These drawbacks are obviated by converting the fats or fatty acids into methyl or ethyl esters, determining the acetyl values of these esters, and calculating the result into the corresponding values for the fatty acids or glycerides.[93]

By using carbon tetrachloride instead of glacial acetic acid as the solvent for the iodine chloride a solution much richer than the ordinary Wijs solution is obtained. From 30 minutes to 2 hours is required for the complete absorption of the halogen by fats, and the results agree with those obtained by Hübl's method.[94]

Glycerol.

From a comparison of the recorded values for the sp. gr. of pure glycerol with those obtained with glycerol purified with special precautions, the conclusion is drawn that the table of Gerlach[95] is the most trustworthy for determining the amount of glycerol from the sp. gr. For estimating small quantities of water in glycerin the boiling-point method affords the most accurate means, the presence of 1%

[91] C. E. Scholl, *J. Ind. Eng. Chem.*, 1919, **11**, 842 ; *J.*, 1919, 778A.
[92] L. Carcano, *Boll. Chim. Farm.*, 1919, **58**, 121 ; *J.*, 1919, 687A.
[93] A. Grün, *Oel- u. Fettind.*, 1919, **1**, 339, 364 ; *J.*, 1920, 33A.
[94] E. Hildt, *Rev. Prod. Chim.*, 1918, **21**, 254 ; *J.*, 1919, 589A.
[95] *J.*, 1885, 226.

of water lowering the boiling point of pure glycerol from 290° C. to
239° C.[96] Other determinations of the specific gravity and refractive
power of glycerin solutions have also given results in close agreement
with Gerlach's table.[97]

LEATHER, ETC.

Furfural may be used as a reagent in the analysis of tannins, since
it combines with them to form compounds similar to those formed
by the action of formaldehyde on tannin.[98] The "furfural precipita-
tion value" is obtained by separating the precipitate and determining
its amount. The filtrate from the precipitate gives a colour reaction
with iron alum and sodium acetate, and the difference in the colorations
obtained enables pyrogallol tannins to be detected in the presence of
catechol tannins.[99] An addition has been made to the Report of
the American Leather Chemists' Association,[100] in which the methods
for the estimation of the total, soluble, and insoluble ash in leather are
discussed in the light of replies received concerning the main report.
It is pointed out that the differences obtained in the determination of
the insoluble ash from the water-soluble substances must be attributed
to variations in the reduction of the magnesium sulphate.[101]

Attention may also be directed to a scheme for the analysis of artificial
leather and its substitutes, in which the various constituents are separ-
ated into groups by successive treatment with different solvents.[102]

ORGANIC PRODUCTS, MEDICINAL SUBSTANCES, ESSENTIAL OILS.

Alkaloids.

A rapid method of determining alkaloids is to liberate them by means
of alkali from an acid aqueous solution, to mix the precipitate and
solution into a soft paste with plaster of Paris, and to extract the alka-
loids from this by means of chloroform. The alkaloid is extracted from
the chloroform solution with standard hydrochloric acid and the
excess of acid titrated.[103] Falières' method of precipitating alkaloids
by means of cuprammonium solution [104] involves the necessity of fre-
quent filtration and restandardisation of the reagent. This may be
obviated by using sufficient ammonia to keep the copper hydroxide
in solution. Titration with the reagent is satisfactory in the case of

[96] A. Grün and T. Wirth, Z. angew. Chem., 1919, 32, 59; J., 1919, 295A.
[97] H. Wolff, Z. angew. Chem., 1919, 32, 148; J., 1919, 470A.
[98] J., 1918, 342A.
[99] R. Lauffmann, Ledertechn. Rund., 1918, 10, 97; J., 1919, 379A.
[100] J., 1917, 472A.
[101] J. Amer. Leather Chem. Assoc., 1919, 14, 443; J., 1919, 732A.
[102] R. Lauffmann, Z. öffentl. Chem., 1918, 24, 212, 239; J., 1919, 227A.
[103] Rapp, Apoth. Zeit., 1918, 33, 463; J., 1919, 336A.
[104] J., 1899, 869.

pure alkaloids, but cannot be used for tinctures, etc. At best, it is less sensitive than the iodeosine method.[105]

Morphine and its salts combine with diazonium compounds in alkaline solution to form characteristic dyes. Diazobenzenesulphonic acid is a suitable reagent for the test, and is capable of detecting less than 1 part in 10,000 of the alkaloid. The method is also applicable to the colorimetric estimation of morphine in presence of other alkaloids.[106]

A comparative study of the methods of estimating morphine has shown that the alkaloid may be completely extracted by a mixture of 2 parts of chloroform and 1 part of alcohol. Sulphuric acid and acetic acid interfere with the reactions of morphine, and should not be present, but hydrochloric and salicylic acids have no such influence.[107] A method is described for the application of this process to the estimation of morphine present as a simple salt in pills, powders, etc.,[108] but resinous constituents interfere with the separation of the alkaloid from opium. These are extracted together with the morphine, then separated by means of salicylic acid, and the alkaloid purified by re-solution and extraction with the solvent.[109]

Experiments have shown that the solubility of morphine in ammonia solution is proportional to the concentration of hydroxyl ions in the liquid. The amount of ammonia required for complete precipitation of morphine is 1·75 times the theoretical quantity, and in practice it is advisable to use twice the quantity and to apply an empirical correction to the weight of morphine obtained by the official German Pharma-copœia method. Meconic acid, which is present in opium, does not interfere with the estimation of the morphine.[110]

Berberine may be accurately estimated in an alcoholic extract of *Hydrastis canadensis* by precipitation with Mayer's reagent (mercuric chloride and potassium iodide). The precipitate is extracted with ether in presence of sodium chloride, an excess of an ethereal solution of picrolonic acid added to the extract, and the berberine picrolonate washed with ether, dried at 110° C., and weighed. The relatively small quantities of canadine and meconine present are negligible. For the separation of berberine and hydrastine Mayer's reagent may be re-placed by an aqueous solution of potassium iodide, which precipitates berberine hydriodide.[111]

[105] H. Kunz-Krause and R. Richter, *Arch. Pharm.*, 1917, **255**, 507 ; *J.*, 1919, 737A.
[106] L. Lautenschläger, *Arch. Pharm.*, 1919, **257**, 13 ; *J.*, 1919, 438A.
[107] A. Tingle, *Amer. J. Pharm.*, 1918, **90**, 689 ; *J.*, 1919, 27A.
[108] *Ibid.*, 788 ; *J.*, 1919, 54A;   [109] *Ibid.*, 851 ; *J.*, 1919, 119A.
[110] A. Heiduschka and M. Faul, *Arch. Pharm.*, 1917, **255**, 441, 482 ; *J.*, 1919, 737A.
[111] R. Wasicky and H. Joachimowitz, *Arch. Pharm.*, 1917, **255**, 497 ; *J.*, 1919, 737A.

Pyramidone, Glucosides.

A delicate test for pyramidone has been based upon its reaction with an acid solution of potassium ferricyanide and ferri chloride to form Prussian blue. Under the same conditions antipyrin gives a blood-red coloration (or yellow, in the presence of hydrochloric acid), and the test is capable of detecting 0·01 part of pyramidone in presence of 1 part of antipyrin. No colour reaction is given by phenacetin, acetanilide, acetylsalicylic acid, methylacetanilide, or caffeine. The method has also been extended to the detection of various substances of vegetable origin (glucosides, etc.), many of which give the distinctive blue reaction.[112] Substances containing oxidases or peroxidases give a violet coloration when treated with the reagent and pyramidone, and the colour is intensified by the addition of hydrogen peroxide. On then adding α-naphthol a wine-red coloration is produced quite distinct from that given by β-naphthol, so that the reaction may be used to distinguish between the two naphthols.[113]

Saccharin.

From a comparative study of the methods of determining saccharin the conclusion has been drawn that trustworthy results can only be obtained by the method of hydrolysis with dilute sulphuric acid and by the method of Richmond and Hill (J., 1918, 246r).[114]

Alcohol, Ether, etc.

It is not possible to estimate a small amount of ether in alcohol by determining the sp. gr. of the liquid, since although each 1% of ether lowers the sp. gr. by 0·0007 the presence of 0·25% of water will mask the presence of the ether. This difficulty may be obviated by concentrating the ether by distillation, determining the sp. gr. of the alcohol before and after distillation, and calculating the amount of ether by means of a formula.[115]

A method has been devised for the estimation of ethyl alcohol, aldehyde, and acetone in admixture, in which the aqueous distillate is oxidised in the cold with chromic acid, the excess of the latter reduced with ferrous sulphate, the liquid distilled into sodium hydroxide solution, and the distillate redistilled with hydroxylamine hydrochloride. The acetone, which is not oxidised by the chromic acid, reacts with the hydroxylamine to form a ketoxime, whilst an equivalent quantity of hydrochloric acid is liberated, and on titration affords a measure of the amount of acetone. A further portion of the original solution

[112] L. P. J. Palet, Anal. Soc. Quim. Argentina, 1918, 6, 151, 156; J., 1919, 54A, 55A.   [113] Ibid., 250; J., 1919, 55A.
[114] O. Beyer, Chem.-Zeit., 1919, 43, 537; J., 1919, 844A.
[115] H. E. Cox, Analyst, 1919, 44, 26; J., 1919, 117A.

is treated with hydroxylamine hydrochloride, which reacts with the aldehyde and acetone, and the free acidity is again titrated. Alcohol and aldehyde are oxidised together in a third portion and the amount of chromic acid corresponding to the aldehyde is deducted.[116]

Chloroform.

Free hydrochloric acid in chloroform may be detected by adding a trace of p-dimethylaminoazobenzene, which gives a violet-red coloration with acid samples. The test is very sensitive and is not given by carbon dioxide or anhydrous formic or acetic acid in chloroform solution.[117]

[116] K. Hoepner, *Z. Unters. Nahr. Genussm.*, 1917, **34**, 453 ; *J.*, 1919, 735A.
[117] D. Vorländer, *Ber. deuts. pharm. Ges.*, 1918, **28**, 385 ; *J.*, 1919, 55A.

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SUBJECT INDEX.

ABBREVIATIONS USED IN FOOTNOTES.

THE following is a list of journals, &c., to which reference is made in this volume, with the abbreviations used. Where the title has not been abbreviated it is given in the first column only.

Abs. Bacteriol.	.	Abstracts of Bacteriology.
Aerial Age Weekly.		
Agric. Bull. F.M.S.	. .	Agricultural Bulletin of the Federated Malay States.
Agric. J. India	.	Agricultural Journal of India.
Agric. Res. Inst. Pusa Indigo Pub.	.	Agricultural Research Institute, Pusa, Indigo Publications.
Alkali Inspector's Rep.	. .	Reports of the Chief Inspector under the Alkali Works Act.
Allg. Brau. u. Hopfenzeit.		Allgemeine Brau- und Hopfenzeitung.
Allg. Z. Bierbrau. u. Malzfabr.		Allgemeine Zeitschrift fur Bierbrauerei und Malzfabrikation.
Amer. J. Dis. Children	.	American Journal of the Diseases of Children.
Amer. J. Pharm.	.	American Journal of Pharmacy.
Amer. J. Physiol.	.	American Journal of Physiology.
Amer. J. Sci.	.	American Journal of Science.
Amer. Silk J.	.	American Silk Journal.
Anal Fis. Quim.	.	Anales de la Sociedad Española Fisica y Quimica.
Anal. Soc. Quim. Argentina	. .	Anales de la Sociedad Quimica Argentina.
Analyst.		
Annalen	. .	Justus Liebig's Annalen der Chemie.
Ann. Bot.	. .	Annals of Botany.
Ann. Chim. . .	.	Annales de Chimie.
Ann. Chim. Analyt.	. .	Annales de Chimie Analytique.
Ann. Falsif.	.	Annales des Falsifications.
Ann. Inst. Pasteur	.	Annales de l'Institut Pasteur.
Ann. Mines de Belgique.		Annales des Mines de Belgique.
Ann. Musée Colon. Marseille	.	Annales du Musée Coloniale de Marseille.
Annali Chim. Appl.	.	Annali di Chimica Applicata.
Ann. Rep.	. .	Annual Reports of the Progress of Applied Chemistry.
Ann. Rep. Rothamsted Expt. Sta.	.	Annual Reports of Rothamsted Experiment Station.
Apoth.-Zeit.	.	Apotheker-Zeitung.
Arb. Reichsgesundheitsamte		Arbeiten aus dem Reichs-Gesundheitsamte.
Arch. Exp. Path. Pharm.		Archiv fur experimentelle Pathologie und Pharmakologie.
Arch. Hyg. .	.	Archiv für Hygiene.
Arch. Pharm.	.	Archiv der Pharmazie.
Archief Suikerind. Ned. Indië		Archief voor de Suikerindustrie in Nederlandsch-Indië.
Ark. Kem., Min., o. Geol.		Arkiv for Kemi, Mineralogi, och Geologi.
Arms and Explosives.		

Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Aus. Chem. Eng. and Min. Rev.	Australian Chemical Engineering and Mining Review.
Baumaterialenkunde.	
Bergbau und Hütte.	
Ber.	Berichte der deutschen chemischen Gesellschaft
Ber. deutsc Pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt fur Agrikulturchemie und rationeller Landwirtschafts-Betrieb.
Biochem. J.	Biochemical Journal.
Biochem. Zeits.	Biochemische Zeitschrift.
Blast Furnace and Steel Plant.	
Bd. of Trade J.	Board of Trade Journal.
Boll. Chim. Farm.	Bolletino Chimico Farmaceutico.
Brasserie et Malterie.	
Brau- u. Malzind.	Brau- und Malzindustrie.
Brennereizeit.	Brennereizeitung.
Brewers' J.	Brewers' Journal.
Brewing Trade Review.	
Brit. J. Phot.	British Journal of Photography.
Bull. Agric. Intell.	Bulletin of Agricultural Intelligence and Plant Diseases.
Bull. Amer. Inst. Min. Eng.	Bulletin of the American Institute of Mining Engineers.
Bull. Assoc. Ind. Laniera Ital.	Bulletino dell' Associazione dell' Industria Laniera Italiana.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association Chimique de Sucre et de Distillerie.
Bull. de l'Office Coloniale.	Bulletin de l'Office Coloniale.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. Agric. France.	Bulletin de la Société Agricole de France.
Bull. Soc. Chim.	Bulletin de la Société Chimique de France.
Bull. Soc. Chim. Belg.	Bulletin de la Société Chimique de Belgique.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie.
Bull. Soc. d'Encour.	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. Ind. Min.	Bulletin de la Société de l'Industrie Minière.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Canad. Chem. J.	Canadian Chemical Journal.
Can. Machinery	Canadian Machinery
Can. Min. Inst. Bull.	Canadian Mining Institute Bulletin.
Can. Min. J.	Canadian Mining Journal.
Caoutchouc et Guttapercha.	
Centr. Bakt.	Centralblatt für Bakteriologie.
Chem. Age	Chemical Age.
Chemical Engineer.	
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. News	Chemical News.
Chem. Soc. Trans.	Transactions of the Chemical Society.
Chem. Trade J.	Chemical Trade Journal.
Chem. Umschau	Chemische Umschau ueber die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem.-Zeit.	Chemiker-Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Chim. et Ind.	Chimie et Industrie.
Circ. Paint Manufrs. Assoc. U.S.	Circulars of the Paint Manufacturers Association of the United States.
Coal Age.	
Collegium.	
Comptes rend.	Comptes rendus hebdomadaire des Séances de l'Academie des Sciences.

Comptes rend. Trav. Lab, Carlsberg — Comptes rendus des Travaux de Laboratoire de Carlsberg.

Colliery Guardian.

Comm. Central Rubber Stat. Buitenzorg — Communications of the Central Rubber Station, Buitenzorg, Java.

Comm. Netherland Govt. Inst. for advising Rubber Trade — Communications of the Netherland Government Institute for Advising the Rubber Trade and Rubber Industry.

Contract Record and Engineering Review.

Dépêche Col. . . — Dépêche Coloniale.

Deuts. Essigind. . . — Deutsche Essigindustrie.

Deuts. Med. Woch. . — Deutsche Medizinische Wochenschrift.

Do Veldbode.

Dyer.

Edinburgh Review.

Elect. Rev. . . . — Electrical Review.

Electrician.

Elektrotechn. Zeits. . — Elektrotechnische Zeitschrift.

Engineering.

Eng. and Min. J. . . — Engineering and Mining Journal.

Eng. Rev. . . . — Engineering Review.

Explosives.

Faraday Soc. . . — Faraday Society.

Farben-Zeit. . . — Farben-Zeitung.

Färber-Zeit. . . — Farber-Zeitung.

Fermentforsch. . . — Fermentforschung.

Ferrum.

Finska Kemistsamfundets Meddelingen.

Gas Age.

Gas J. . . . — Gas Journal.

Gas World.

Gaz. Chim. Ital. . . — Gazzetta Chimica Italiana.

Gerber.

Ges Abhandl. Kennt. Kohle . . . — Gesammelte Abhandlungen zur Kenntniss der Kohle.

Gluckauf.

Helv. Chim. Acta . — Helvetica Chimica Acta.

Ind. Engineering . — Indian Engineering.

Ind. J. Med. Res. . — Indian Journal of Medical Research.

Indiarubber J . — Indiarubber Journal.

Indiarubber World.

Inst. Min. and Met. . — Institution of Mining and Metallurgy.

Inst. Pet. Tech. . — Institution of Petroleum Technologists.

Int. Military Digest . — International Military Digest.

Intern. Sugar J. . . — International Sugar Journal.

Iron Age.

Iron and Coal Trades Rev. — Iron and Coal Trades Review.

Iron and Steel Inst. Carnegie Schol. Mem.. — Iron and Steel Institute, Carnegie Scholarship Memoirs.

Jap. Med. Literature . — Japanese Medical Literature.

J. . . . . — Journal of the Society of Chemical Industry.

J. Agric. Res. . . — Journal of Agricultural Research.

J. Agric. Sci. . . — Journal of Agricultural Science.

J. Amer. Ceram. Soc. — Journal of the American Ceramic Society.

J. Amer. Chem. Soc. — Journal of the American Chemical Society.

J. Amer. Leather Chem. Assoc. . . . — Journal of the American Leather Chemists Association.

J. Amer. Soc. Mech. Eng. — Journal of the American Society of Mechanical Engineers.

J. Biol. Chem. . . — Journal of Biological Chemistry.

J. Bd. Agric. . . — Journal of the Board of Agriculture.

J. Chem. Ind Tokyo . — Journal of Chemical Industry, Tokyo

J. Chem. Met. and Min. Soc. S. Afr.	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Four Elect. . .	Journal du Four Electrique.
J. Franklin Inst. . .	Journal of the Franklin Institute.
J. Gasbeleucht. . .	Journal für Gasbeleuchtung.
J. Gen. Physiol. .	Journal of General Physiology.
J. Ind. Eng. Chem. .	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing .	Journal of the Institute of Brewing.
J. Inst. E. E. .	Journal of the Institution of Electrical Engineers.
J. Inst. Mech. Eng.	Journal of the Institution of Mechanical Engineers.
J. Iron and Steel Inst	Journal of the Iron and Steel Institute.
J. Landw. . .	Journal für Landwirtschaft.
J. Path. and Bact.	Journal of Pathology and Bacteriology
J. Pharm. Chim. .	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan .	Journal of the Pharmaceutical Society of Japan.
J. Phys. Chem. . .	Journal of Physical Chemistry.
J. prakt. Chem .	Journal fur praktische Chemie.
J. Proc. Royal Soc. N.S. Wales	Journal and Proceedings of the Royal Society of New South Wales.
J. Roy. Army Med. Corps	Journal of the Royal Army Medical Corps.
J. Roy. Soc. Arts . .	Journal of the Royal Society of Arts.
J. Soc. Dyers and Col. .	Journal of the Society of Dyers and Colourists.
J. Soc. Glass Tech. .	Journal of the Society of Glass Technologists.
J. Soc. Leather Trades Chem. . . .	Journal of the Society of Leather Trades Chemists.
J. Text. Inst. .	Journal of the Textile Institute.
J. Wash. Acad. Sci	Journal of the Washington Academy of Sciences.
Ker. Rundschau . .	Keramische Rundschau.
Koll.-Chem. Beih. .	Kolloid-Chemische Beihefte.
Kolloid Zeits. . .	Kolloid Zeitschrift.
Kunststoffe.	
La. Bulletin .	Louisiana Bulletin.
La. Planter .	Louisiana Planter.
Lancet.	
Landw. Versuchs-Stat. .	Die landwirtschäftlichen Versuchs-Stationen."
Le Papier.	
Ledertechn. Runds. .	Ledertechnische Rundschau.
Med. Klinik . . .	Medizinische Klinik.
Mem. Coll. Eng. (or Sci.) Kyoto Imp. Univ.	Memoirs of the College of Engineering (or Science), Kyoto Imperial University.
Metal Ind. . . .	Metal Industry.
Metall u. Erz .	Metall und Erz.
Met. and Chem. Eng. .	Metallurgical and Chemical Engineering.
Metan.	
Midland Drugg. and Pharm. Rev. . .	Midland Druggist and Pharmaceutical Review.
Min. Mag. . . .	Mining Magazine.
Min. and Sci. Press	Mining and Scientific Press.
Mitt. K. Materialprüf. .	Mitteilungen aus dem Koniglichen Materialprufungsamt zu gross-Lichterfelde West.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchungen und der Hygiene.
Monatschr. Textilind. .	Monatschrift fur Textil-Industrie.
Monatsh. Chem. . .	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monit. Scient. . .	Moniteur Scientifique.
Nature.	
N.Z. J. Sci. and Tech. .	New Zealand Journal of Science and Technology.
Oel- u. Fettind. . .	Oel- und Fettindustrie.

Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Oil and Colour Chem. Assoc.	Oil and Colour Chemists' Association.
Oil and Gas.	
Optician.	
Paper.	
Papierfab.	Papierfabrikant.
Perf. Essent. Oil Rec.	Perfumery and Essential Oil Record.
Petroleum	Petroleum (German).
Petroleum (Chicago).	
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zentralh.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine and Journal of Science.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci.	Philippine Journal of Science.
Phot. J.	Photographic Journal.
Phot. J. Amer.	Photographic Journal of America.
Phot. Korr.	Photographische Korrespondenz.
Physiol. Abs.	Physiological Abstracts.
Proc. Amer. Soc. Testing Materials	Proceedings of the American Society for Testing Materials.
Proc. Cleveland Inst. Eng.	Proceedings of the Cleveland Institute of Engineers.
Proc. K. Akad. Wetensch.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Edition).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Soc. Exp. Biol. and Med.	Proceedings of the Society of Experimental Biology and Medicine.
Pulp and Paper Mag.	Pulp and Paper Magazine of Canada.
Raw Material.	
Rec. Trav. Chim. Pays-Bas.	Recueil des Travaux Chimiques de Pays-Bas.
Rep. Pub. Health Lab. Cairo	Reports of the Public Health Laboratory, Cairo.
Rev. Gén. d'Elect.	Revue Générale d'Electricité.
Rev. Mét.	Revue de Métallurgie.
Rev. Prod. Chim.	Revue de Produits Chimiques.
Rev. Viticult.	Revue de Viticulture.
Revista Viticolt.	Revista Viticoltura.
Rubber Age and Tire News.	
Russ. Phot. Ber.	Russische Photographische Berichte.
Schweiz. Chem. Zeit.	Schweizerische Chemiker-Zeitung.
Sci. Amer. Suppl.	Scientific American Supplement.
Sci. Proc. Royal Dublin Soc.	Scientific Proceedings of the Royal Dublin Society
Sci. Rep. Tôhoku Imp. Univ.	Science Reports of Tôhoku Imperial University.
Seifenfabr.	Seifenfabrikant.
Sitzungsber. K. Preuss. Akad. Wiss.	Sitzungsberichte der Königlichen Preussischen Akademie der Wissenschaften.
Soil Sci.	Soil Science.
Sprechsaal.	
Stahl u. Eisen.	Stahl und Eisen.
Staz. Sper. Agrar. Ital.	Stazione Sperimentali Agraria Italiana
Sugar.	
Tageszeit. f. Brauerei	Tageszeitung für Brauerei.
Technik u. Ind.	Technik und Industrie.
Teknisk Tidskr.	Teknisk Tidskrift.
Text. Manufr.	Textile Manufacturer.

Text. Merc. . . .	Textile Mercury. .
Text. World J. . .	Textile World Journal.
Tidskrift Kemi . .	Tidskrift for Kemi.
Times Eng. Suppl. .	Times Engineering Supplement.
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society.
Trans. Amer. Electrochem. Soc. . .	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Canadian Min. Inst. . . .	Transactions of the Canadian Mining Institute. .
Trans. Ceram. Soc. .	Transactions of the Ceramic Society.
Trans. Ind. Hort. Soc. .	Transactions of the Indian Horticultural Society.
Trans. Inst. Min. and Met	Transactions of the Institution of Mining and Metallurgy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Tropical Life.	
U.S. Bureau of Mines, Bull. and Tech. Papers	U.S. Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau of Standards.	
U.S. Comm. Rep. . .	U.S. Commerce Reports.
U.S. Cons. Rep. . .	U.S. Consular Reports.
U.S. Geol. Survey	U.S. Geological Survey.
U.S. Naval Inst. Proc. .	U.S. Naval Institute Proceedings.
Western Brewer.	
Western Soc. Eng.. U S A.	Western Society of Engineers, U.S.A.
Woch. Brau.. . .	Wochenschrift für Brauerei.
Z. angew. Chem. . .	Zeitschrift fur angewandte Chemie.
Z. anorg. Chem. . .	Zeitschrift der anorganischen Chemie.
Zeits. Biol. . .	Zeitschrift fur Biologie.
Z. Elektrochemie . .	Zeitschrift fur Elektrochemie und angewandte physikalische Chemie.
Z. ges. Brauw. . .	Zeitschrift für das gesammte Brauwesen.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
Z. Gewerbehygiene .	Zeitschrift für Gewerbehygiene.
Z. öffentl. Chem. . ,	Zeitschrift für öffentliche Chemie.
Z. physik. Chem. . .	Zeitschrift für physikalische Chemie.
Z. physiol. Chem. . .	Hoppe-Seyler's Zeitschrift fur physiologische Chemie.
Z. Spiritusind. ,,. .,. .	Zeitschrift für Spiritusindustrie.
Z. Sauerst.-u. Stickstoffind.	Zeitschrift fur Sauerstoff- und Stickstoffindustrie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs und Genussmittel.
Z. Ver. deuts. Zuckerind.	Zeitschrift des Vereins deutscher Zuckerindustrie.
Z. wiss. Phot. . .	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie.
Z. Zuckerind. Böhm. .	Zeitschrift für Zuckerindustrie in Böhmen.